3A.7 CATACARB

Licensor

Eickmeyer and Associates
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State of Development

The CATACARB process uses catalytically aided hot potassium carbonate to remove acid gases by chemical absorption. CATACARB solution contains catalysts to promote the absorption-desorption reactions, and corrosion inhibitor is also added to the solution.

At present, there are 100 CATACARB plants in operation, with a total acid gas removal capacity of 126,400 tpd.[1] [2] Ten more plants are either under construction or in the planning stage.[pc]

Process Description[1] [3]

The use of split streams of lean solution and the omission of a rich/lean solutions exchanger are the major differences between the CATACARB process and other chemical absorption processes described in this Handbook.

In the CATACARB process Figure 3A.7-1), sour raw gas is scrubbed in a packed or trayed tower with a potassium salt solution containing active, stable, non-toxic catalyst. The absorber is often designed with two stages. The sour gas is first scrubbed by a semi-lean solution at the lower stage. The gas is further scrubbed by lean solution when it ascends to the upper stage of the absorber. Purified gas leaves the top of the absorber column. Acid gas rich solution is let down through the power recovery turbine before it is fed to the top of the regenerator, where steam is used to strip the CO_2 and H_2S from it. Steam generated in the reboiler provides heat for regeneration. The regenerated lean solution is partially cooled before it is pumped to the top of the absorber.

The semi-lean solution taken from the middle section of the regenerator contains higher residual acid gases than the lean solution. This split-stream two-stage absorption arrangement can achieve high purity of the gas with good steam economy by providing greater concentration gradient difference of the acid gas components between gas and liquid phases.

Chemical Description[4] [5]

The absorption rate of potassium carbonate solution increases with the temperature. The catalyst additive promotes the chemical reaction rates in both the absorption and regeneration steps. This enables the CATACARB solution to be regenerated to a much lower level than is found in the ordinary hot-potassium carbonate process. The absorption-regeneration steps are as follows:

$$K_2CO_3 + CO_2 + H_2O \longleftrightarrow 2KHCO_3$$
$$K_2CO_3 + H_2S \longleftrightarrow KHCO_3 + KHS$$

From the above reactions, it can be seen that equilibrium relationships have to be maintained in the system. If H_2S is the only acid gas to be absorbed, some CO_2 may be released with H_2S for each absorption-regeneration cycle. Most of the potassium in the solution would eventually be converted to potassium bisulfide, which is essentially non-regenerable, according to the following reaction:

$$2KHS \longleftrightarrow K_2S + H_2S$$

Accordingly, makeup solution may have to be added in a batch or continuous ordinary hot potassium carbonate process. When treating sour gas, the CATACARB process used additives to avoid this problem and thus requires no extra solution makeup.

The CATACARB process can also remove carbon disulfide and carbonyl sulfide without significant solution degradation. Carbonyl sulfide hydrolizes in the process solution:

$$COS + H_2O \longleftrightarrow CO_2 + H_2S$$

The product of the hydrolizing reaction reacts with the potassium carbonate. Mercaptans react with CATACARB solution, with the majority being removed.

Operating Limits[2]

The CATACARB process can be operated at various pressures. The absorption pressure may vary from 40 to 1,000 psig, depending on the operation of a specific plant. The absorption temperature may also vary from 100° to 260 °F. The upper stage of the absorber is operated at low temperature, while the lower stage, where bulk acid gases are removed, is operated at a higher temperature.

Typical acid gas compositions treated in the hydrogen, ammonia, and SNG plants are 15-30%. This range is 5-50% acid gas for natural gas sweetening applications. Concentration of CATACARB solution is normally 20-30% by wt.

Purification Limits

The hot potassium carbonate process has been used to remove carbon dioxide and hydrogen sulfide from a number of gas mixtures. This process can reduce hydrogen sulfide in natural gas to about 4 ppm and the CO_2 content to as low as 50 ppm when gas is under sufficient pressure.

Utility Requirements[pc]

Utility requirements vary widely, depending on whether or not a low heat process cycle is used and on the partial pressure of the CO_2 in the feed gas. The typical ranges per lb mole of CO_2 are

Cooling Water, gal/lb mole of CO_2	98 - 197
Power, kWh/lb mole of CO_2	0.26 - 0.75
Heat, Btu/lb mole of CO_2	20,000 -50,000

Environmental Considerations

Sour acid gases from the stripper require further processing in a sulfur recovery unit.

Remarks

The CATACARB process catalytically purifies feed gas containing CO_2, H_2S, and COS. The solubility of hydrocarbons present in the feed gas is very small in the CATACARB solution. Sour acid gas streams from the process will need further processing to recover sulfur.

References

1. "Gas Processing Handbook," Hydrocarbon Processing, April 1979, p. 110.
2. Eickmeyer, A.G., "Thirty-nine Catacarb Process Plants are Now Sweetening Sour Natural Gas," Oil & Gas Journal, August 9, 1971, pp. 74-75.
3. Morse, J., "Catacarb CO_2 Cuts Costs, Enjoys Big Growth," Oil and Gas Journal, April 22, 1968, pp. 184-185.
4. Riesenfeld, F.C., and Kohl, A.L., "Gas Purification," Gulf Publishing Co., 1974, pp. 175-207.
5. Maddox, R.N., "Gas and Liquid Sweetening," John M. Campbell, 121 Collier Drive, Norman, Oklahoma 73069, April 1977.

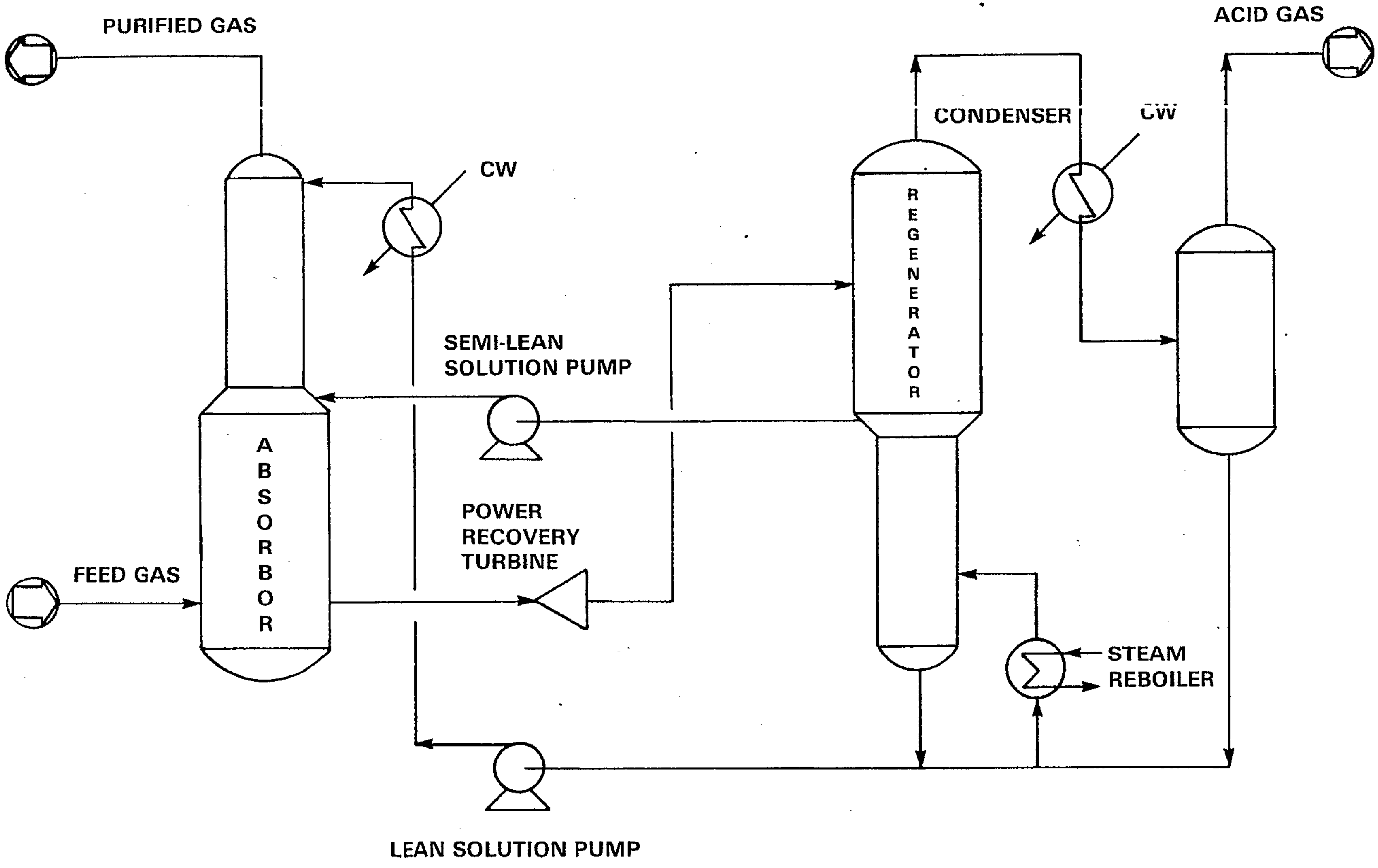

Figure 3A.7-1 Catacarb Process.

3A.8 CARL STILL

Licensee

Dravo Corporation
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Pittsburgh, PA 15222

State of Development[pc]

The Carl Still process was developed by Firma Carl Still GmbH & Co. KG in Germany for the removal of NH_3 and H_2S from coke oven gas. Commercial plants using this process are in operation in Europe and Japan. One plant in Germany has a capacity of 150 MM scfd. Currently, there are three plants running in the United States, and one is under construction.

Since the Carl Still process uses an aqueous NH_3 solution to remove H_2S and since NH_3 is produced in coke oven operations, this process is particularly suited to purification of coke oven gas.

Process Description[1]

Gas enters the H_2S absorber, where it is contacted with aqueous ammonia liquor. The liquor absorbs H_2S to form ammonium sulfide. This reaction is faster than the reaction with CO_2, and the contact time is kept sufficiently short to make the process selective for H_2S.

As shown on the flow diagram (Figure 3A.8-1) there are two sources of ammonia liquor: the NH_3 absorber and the deacifier (deacid-gasifier). The concentration of ammonia in the liquor from the deacifier normally contains about 2% ammonia. Gas leaving the H_2S absorber enters the NH_3 absorber, where the NH_3 content of the gas is reduced to about 3 grains/100 scf (approx. 100 ppm) by scrubbing normally with excess flushing solutions and water. The purified coke oven gas leaves at the top of the column. As an alternative, the gas leaving the H_2S absorber can be treated in a PHOSAM type ammonia removal system (see Chapter 3B.3). A small portion of higher concentrated ammonia can then be used in the H_2S absorber, resulting in a lower concentration of H_2S in the purified gas.

Rich liquor from the H_2S absorber is pumped to the deacifier, where H_2S, NH_3, CO_2, and HCN are stripped by two vapor streams from the NH_3 still. A portion of the stripped liquor from the deacifier is sent to the ammonia still for NH_3 separation by distillation for subsequent NH_3 recovery. The remainder of the stripped liquor is returned to the H_2S absorber.

The NH_3 in the gas stream leaving the deacifier can be recovered as ammonium sulfate by treatment with sulfuric acid or as anhydrous ammonia by using the PHOSAM process. The H_2S can be converted to either elemental sulfur or sulfuric acid. Firma Carl Still, the developer of the process, has a reactor designed to pretreat the incoming H_2S rich gas to catalytically destroy any HCN, NH_3, and hydrocarbons in the gas before it enters the Claus plant. This contributes toward trouble-free operation of the Claus plant.

Chemical Description

The H_2S and some of the HCN and CO_2 in the coke oven gas are removed by chemical absorption in the aqueous ammonia solution as shown in the following reactions[pc]

$$NH_3 + H_2S \longleftrightarrow NH_4SH \text{ (aqueous)}$$
$$NH_3 + HCN \longleftrightarrow NH_4CN \text{ (aqueous)}$$
$$NH_3 + H_2O + CO_2 \longleftrightarrow NH_4HCO_3 \text{ (aqueous)}$$

Ammonia recovery in the column following the H_2S absorber involves physical absorption of gaseous ammonia in water:

$$NH_3 + H_2O \longleftrightarrow NH_4OH$$

The combined streams from both absorbers are then fed to the deacifier stripper, where the above reactions are reversed to free the NH_3, HCN, H_2S, and CO_2.

Operability Limits

The Carl Still process normally operates at near atmospheric pressure. A higher-pressure operation is more advantageous, and a 130 MM scfd plant in the Netherlands operates at 10 psig. Gas entering the H_2S absorber should be cooled to approximately 86 °F to enhance absorption of H_2S and NH_3.

The Carl Still process can handle the H_2S, HCN, and NH_3 concentrations normally encountered in coke oven gas. Since this process depends on the NH_3 in the gas for its purification action, it could not be used, in its present form, to purify coal conversion gases with uncommonly low NH_3 concentrations.

Purification Limits

The H_2S content of the gas leaving to the Carl Still process can be reduced to 10 grains/100 scf and the NH_3 content can be lowered to less than 3 grains/100 scf (approx. 100 ppm). Organic sulfides such as COS and CS_2 are not normally removed by this process. However, Firma Still has developed a process in conjunction with light oil removal that removes and recovers the majority of these compounds. Approximately 50% of the HCN is removed.

Utility Requirements

The following utility requirements are estimated per MM scf of coke oven gas containing 390 grains H_2S/100 scf (approx. 0.6 vol%) and 300 grains NH_3/100 scf (approx. 1 vol%). H_2S and NH_3 contents of the feed gas are lowered to 35 grains/100 scf (approx. 560 ppm) and 4 grains/100 scf (approx. 130 ppm), respectively. Included in the following utilities is the treatment of the excess flushing liquor, estimated at 2500 gal/MM scf. The recovered NH_3 is converted to $(NH_4)_2SO_4$ in an indirect saturator, and the H_2S converted to elemental sulfur in a Claus plant.

L.P. Steam, lb/MM scf	10,000
Cooling Water, gal/MM scf	70,000
Boiler Feed Water, gal/MM scf	160
Electric Power, kWh/MM scf	150
Sulfuric Acid (66 ° BE), lb/MM scf*	1,500

* H_2S could be recovered as sulfuric acid (60 ° BE or 66 ° BE) for use in ammonium sulfate production and eliminate this raw material requirement.

Battery limits for the above utility requirements include the basic Carl Still process and a Claus plant.

Environmental Considerations

The Carl Still process is designed to remove primarily H_2S using the NH_3 contained in the coke oven gas. Therefore, it is operated in conjunction with an NH_3 recovery (or destruction) process and a H_2S conversion process. No external reagents are necessary for desulfurization; therefore no accompanying wastewater problems are generated.

Remarks

The Carl Still process was developed for the treatment of coke oven gas at atmospheric pressure. Since the process uses an NH_3 solution to absorb the H_2S, it is suited for treatment of gases containing NH_3. Gases containing NH_3 from coal gasification facilities could conceivably be treated by this process.

References

1. "Hydrogen Sulfide/Ammonia Removal from Coke Oven Gas," Bulletin, Dravo Corporation, 1974.

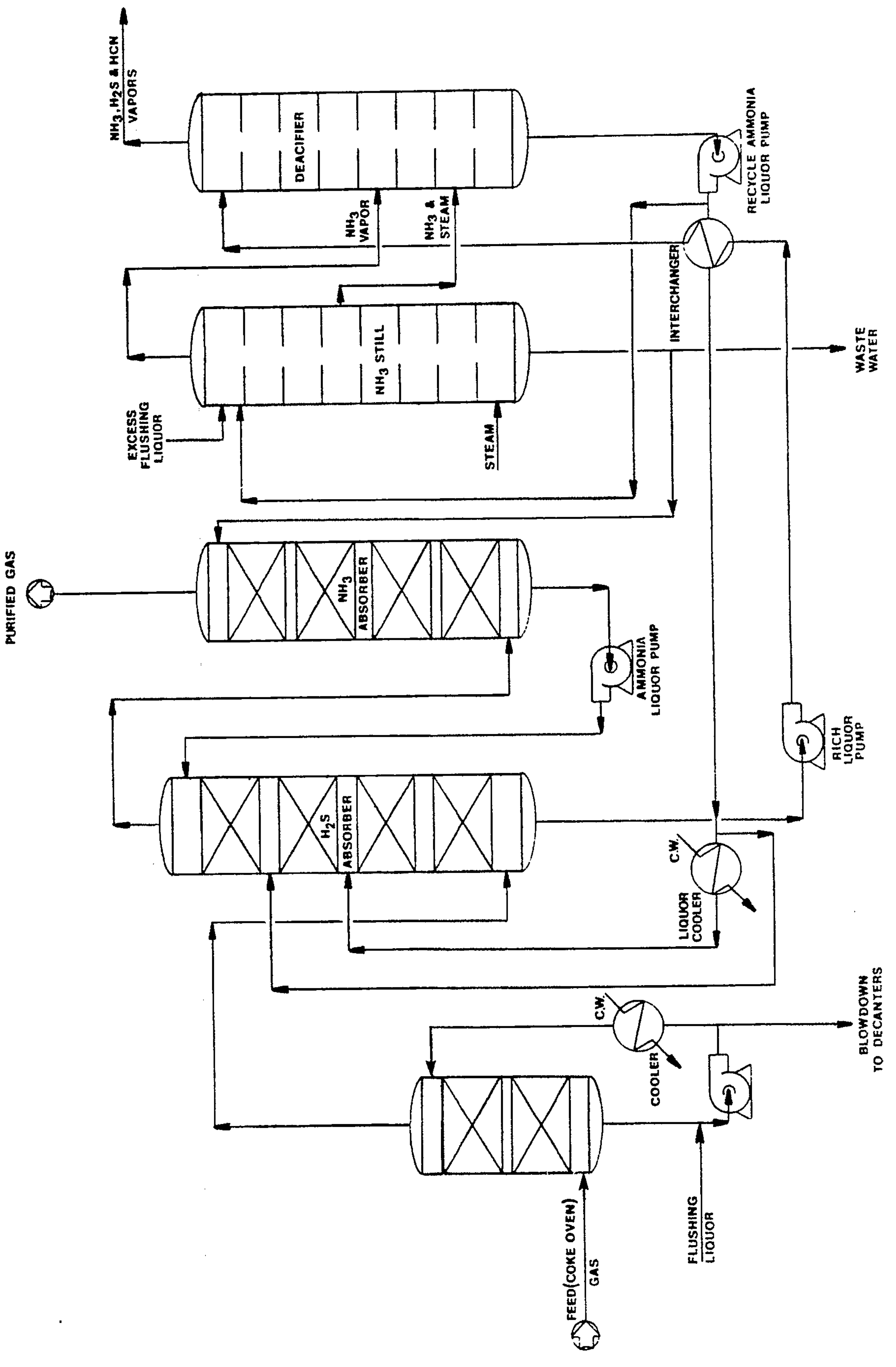

Figure 3A.8-1 Carl Still Process.

3A.9 CLAUS

Licensor

The basic Claus process was developed in the late nineteenth century. Since that time, many modifications have been made in the process by various engineering firms. Some of the firms currently active in this field include:

1. Black, Sivalls and Bryson, Inc.
   B.S.& B. Process Systems Division
   8303 South West Freeway
   Houston, TX 77074

2. Ford, Bacon & Davis (Texas), Inc.
   P.O. Box 38209
   Dallas, TX 75238

3. Ralph M. Parsons Company
   100 W. Walnut St.
   Pasadena, CA 91124

State of Development[1] [2]

The Claus process has undergone a number of modifications since it was first disclosed by Claus in 1883. Today, many commercial plants having sulfur capacities of 5 to 1650 tpd are in operation Complete conversion of H_2S to elemental sulfur is not possible because of the equilibrium relationships of the chemical reactions upon which the process is based.[1] Therefore, this process may not adequately reduce sulfur compounds to the level required by specific air pollution regulations. For this reason, various add-on processes such as the SCOT (Chapter 3A.18) and Beavon (Chapter 3A.5) have been developed to handle the Claus tail gas.

Process Description[2] [3]

There are two basic forms of the Claus process: (1) the partial combustion process and (2) the split stream process.[1] The partial combustion process is used for gas streams of high (greater than 50%) H_2S content, while the split process may be used for gas streams with less H_2S.

A typical Claus partial combustion process scheme is shown in Figure 3A.9-1. Acid gas entering the plant passes through a knock-out vessel, where any entrained liquids are removed. Gas is then blown into the sulfur burner, where it is mixed with sufficient air to oxidize one third of the H_2S to SO_2 and burn all the other combustibles (hydrocarbons, etc.). The combustion products and the remaining H_2S from the burner enter the reaction furnace, where enough residence time is provided for the Claus reactions (shown in Chemical Description) to come to equilibrium.

Ammonia present in one of the sulfur bearing streams or the main sulfur bearing stream poses a combustion problem. In many refinery and some other process situations, the ammonia will be present in a relatively low volume sour water stripper stream that also contains a quantity of H_2S that must be recovered. Two-step combustion in which the sour water stripper stream is mixed with an excess of oxygen to totally combust the H_2S, the hydrocarbon, and the ammonia, followed by the addition of the main H_2S bearing stream is practiced to handle this problem. It is usually, but not always, successful. When ammonia is present in the main sulfur plant feed stream, careful design of the burner and combustion chamber is requred to achieve the total decomposition of the ammonia under a partial combustion processing arrangement. This is a typical processing problem on coke oven gas and some gases from coal gasification.

Effluent gas from the reaction furnace is cooled in a waste boiler, where steam is generated. Effluent gas from the boiler flows to a condenser, where all the sulfur formed initially is removed and routed to the sulfur rundown tank. Additional low-pressure steam is produced in this and other sulfur condensers shown on the flow diagram.

The temperature of the gas decreases as it passes through the waste heat boiler. At lower temperatures, the equilibrium conversion of H_2S is high, but the rate of conversion is low. To increase the reaction rate, and yet to achieve high conversion, the gas is passed through a series of catalytic reactors.

Effluent gas from the first sulfur condenser must be reheated before entering the first catalytic reactor. There are at least four methods currently in use to reheat the gas from the first condenser to the proper temperature for entering each of the catalytic converters. The earliest system involved bypassing some of the acid gas feed to an additional burner, where the gas was mixed with the proper quantity of air, and these combustion products blended with the gas from the condenser to produce the proper temperature entering the catalytic converter. Two or three of these small burners in addition to the main burner would be used, depending on the number of catalytic converters.

A later innovation, shown in Figure 3A.9-1, has some of the hot combustion gas products from the main burner bypassing most of the waste heat boiler and being available to blend with the gas from the individual sulfur compressors to produce the proper inlet temperature at the catalytic converters.

More popular today is the use of high-pressure steam or hot oil heat exchangers to reheat the gas from each sulfur condenser before it enters the catalytic converter. The entire process stream from the initial combustion process passes through the waste heat boiler to the first condenser and is then reheated before entering the catalyst bed. The cycle of cooling and condensing sulfur, reheating the gas with an exchanger, and passing through the catalyst bed to the next sulfur condenser is repeated for the number of catalyst beds involved. High-pressure steam (550-600 psig) from the available plant utilities or produced in the waste heat boiler can be used as the source of steam. Hot oil produced in an independent hot oil package or from hot loops available at the processing site can be used as the source for hot oil for this reheat method.

Any entrained sulfur in the tail gas leaving the last sulfur condenser is removed in a knock-out vessel. Final tail gas leaving the Claus unit may require further treatment to meet environmental regulations, depending on the industry.

Although Figure 3A.9-1 shows three catalytic reactors, more or less than three stages may also be used. More stages result in a higher sulfur recovery and less sulfur leaving in the tail gas. The exact number of stages is selected by considering the tradeoff between the capital investment and the amount of sulfur leaving in the tail gas.

In the partial combustion process described above, the entire acid gas stream is mixed with a stoichiometric amount of air to burn one-third of the H_2S to SO_2. In the split stream process, one-third of the acid gas is fed to the reaction burner, and all the contained H_2S is burned to SO_2 with stoichiometric air. Hot gases are cooled in a waste heat boiler and then combined with the remaining two-thirds of the gas before entering the first catalytic conversion stage. The split stream process can handle gases with H_2S content as low as about 20%.

Chemical Description[1]

The main chemical reactions taking place in the Claus process are:

$$H_2S + 3/2\ O_2 \longrightarrow H_2O + SO_2 \quad (1)$$

$$2H_2S + SO_2 \xrightarrow{\text{catalyst}} 3S + 2H_2O \quad (2)$$

Reaction (1) takes place in the burner at 2000 to 3000 °F and 1 atm. Reaction (2) takes place at about 200 °F or lower. A lower catalytic stage temperature favors the equilibrium conversion but reduces the reaction rate.

The catalyst used in the Claus process is either natural bauxite or alumina in the form of pellets or balls. The catalyst shape should be designed to minimize the pressure drop incurred at space velocities of 1000 to 2000 volumes of gas per hour per volume of catalyst.[1]

In the partial combustion scheme, small quantities of COS and CS_2 are formed in the reaction furnace, particularly if large amounts of CO_2 are present. These compounds are hydrolyzed in the first catalytic reactor by the following reactions when the temperature is sufficiently high.

$$COS + H_2O \longleftrightarrow CO_2 + H_2S$$
$$CS_2 + 2H_2O \longleftrightarrow CO_2 + 2H_2S$$

In the split stream process, where all the H_2S is burned to SO_2, COS and CS_2 are not formed as readily.

Operability Limits

The Claus process is not a gas purification process in the true sense of the word. The principal objective of the process is the recovery of sulfur from a gas stream that itself is a product of a previous gas purification process. The feed gas to the Claus unit usually consists of H_2S plus inerts. Since the heat for the Claus process is supplied by burning part of the H_2S, the H_2S concentration is the most important parameter in Claus plant operation. Normal H_2S concentrations are 35 vol% and higher. However, gases with concentrations of approximately 20% can be handled in a more or less normal manner. When the H_2S concentration is less than 20%, unusual processing schemes are required, such as using oxygen or oxygen-enriched air for combustion or adding a suitable fuel gas to the gas stream.

Purification Limits

Depending on the H_2S concentration, the number of catalytic stages, and the quality of the catalyst used, conversion efficiencies (% of total sulfur removed) of up to 98% can be attained. In general, the conversion efficiencies would be greater than 94%.

Utility Requirements[pc]

Utility requirements vary widely, depending on feed and processing conditions. As an example, utility requirements per pound of sulfur produced from a gas containing about 40% H_2S and 60% CO_2 are estimated to be:

Steam Generated, lb/lb of sulfur	3.0
BFW, gal/lb of sulfur	0.4
Electric Power, kWh/lb of sulfur	0.04

Environmental Considerations

Since the basic Claus reaction is limited by chemical equilibrium, the tail gas from the Claus unit will normally have sulfur values corresponding to about 15,000 ppm of SO_2. These sulfur values are usually present in the form of H_2S, SO_2, sulfur vapor, and unconverted COS and CS_2. Depending on air quality regulations applying to the particular energy producing plant of which the Claus plant is a part, it may be necessary to treat the Claus tail gas in an add-on facility.

Remarks

Claus is a widely used and dependable process for recovering sulfur from acid gases separated in an absorption/desorption type acid gas removal unit. The sulfur product is 99.9% pure and highly marketable. An additional facility may be necessary to treat the tail gas from the Claus unit.

References

1. Riesenfeld, F. C., and Kohl, A. L., "Gas Purification," 2nd Edition, Gulf Publishing Company, Houston, Texas, 1974.

2. Grancher, P., "Advances in Claus Technology," Hydrocarbon Processing, September 1978, pp. 257-262.

3. "Modified Claus," Hydrocarbon Processing, April 1971, p. 112.

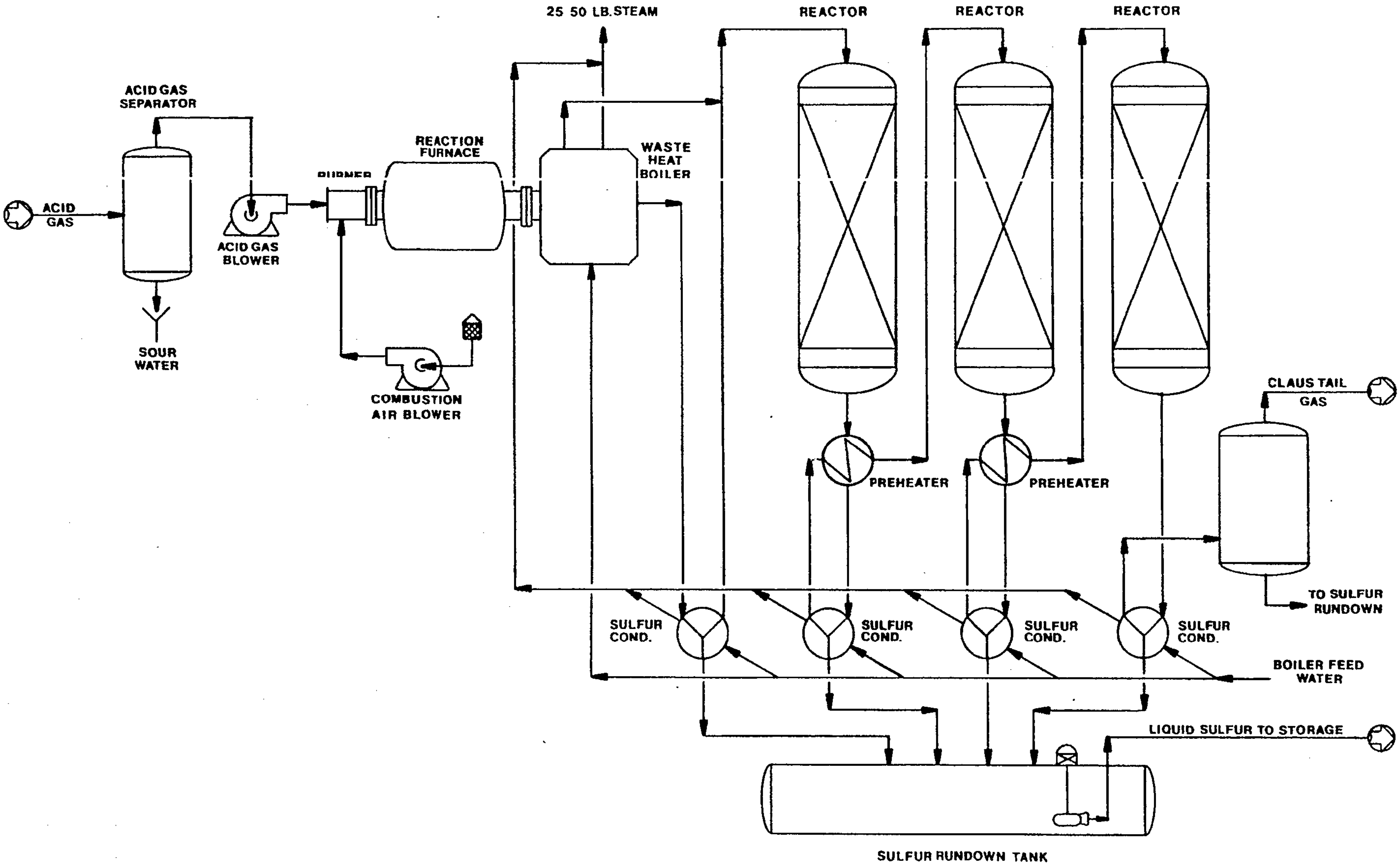

Figure 3A.9-1 Claus Process

3A.10 FLUOR ECONAMINE

Licensor

Fluor Engineers and Constructors, Inc.
Irvine, California

State of Development[1] [2] [3]

The Economine - diglycol amine (DGA) - process for acid gas removal was developed by the Fluor Corporation in 1950. The first commercial Econamine plant was put on stream in 1965. Since then, more than 30 plants using DGA as absorbent have been in operation, processing more than six billion scfd of natural gas. Recently improvements have been made in the process by varying a number of design parameters and revising the flow scheme to take advantage of some of the inherent characteristics of the DGA solution. More than 4 billion scfd of gas will be processed in the Improved Econamine plants.

Process Description[3] [4]

As shown in Fig. 3A.10-1, the sour feed gas is passed through the absorber tower and is contacted by a countercurrent stream of aqueous lean DGA solution. The solution absorbs H_2S and CO_2 from the gas stream.

The purified gas leaves the top of the absorber. The rich DGA solution from the bottom is flashed to release some hydrocarbons that are dissolved in the solution during the countercurrent contact in the absorber. The rich solution is preheated by exchanging heat with the lean solution from the stripper (regenerator) bottoms before entering the top of the stripper. In the stripper, the DGA solution is stripped of its acid gas components by steam generated in the reboiler. The acid gases from the top of the regenerator are passed through a condenser, where most of the water vapor is condensed from the gas stream. The acid gas is converted to elemental sulfur (if H_2S is present) or vented (CO_2 only), and the condensed water is refluxed back to the regenerator.

Low-pressure steam is used in the reboiler to provide heat for the solution regeneration. Stripped lean solution from the regenerator is cooled by exchanging heat with the rich stream and is then further cooled to the desired temperature before being pumped back to the absorber.

The process scheme is very much similar to that used in other amine absorption systems.

Chemical Description[1]

Acidic components in the feed gas stream, such as H_2S, COS, as well as CO_2, are chemically absorbed by DGA ($HO\text{-}C_2H_4\text{-}O\text{-}C_2H_4)NH_2$. DGA is thermally more stable and has a lower vapor pressure at the process conditions than the other amines.

DGA can be used in aqueous solution at concentrations ranging from 5 to 90% by weight. DGA is non-corrosive to carbon steel. The reversible chemical absorption reactions proceed as follows:

$$RNH_2 + H_2S \longleftrightarrow RNH_3 \bullet HS$$

$$RNH_2 + CO_2 + H_2O \longleftrightarrow RNH_3 \bullet HCO_3$$

R denotes ($HO\text{-}C_2H_4\text{-}O\text{-}C_2H_4$)

DGA also reacts with CO_2 and carbonyl sulfide to form urea-type degradation products. These degradation products are thermally reversible at the operating temperature of the reclaimer.

Operability Limits

The regeneration usually operates at 250-280 °F and 5-15 psig. Temperatures in the absorber may range from 90 °F to 220 °F, and there is no upper limit on pressure (although at very high pressures, physical solvents may be more economical - see Fluor Solvent.) The Improved Econamine uses 50-65 wt% of DGA solution. In some cases, acid gas loading approaching the stoichiometric ratio can be treated successfully.

Purification Limits[2]

The process can be designed to reduce the concentration levels of H_2S to less than 4 ppm, and CO_2 to less than 50 ppm. H_2S content in feed gas treated has been as high as 27%. DGA can also remove COS, thus making it possible to eliminate the downstream COS removal process.

Utility Requirements

Utility requirements of the DGA unit are estimated for acid gas concentrations of 5% CO_2, 5% H_2S in the feed gas at a pressure of 850 psig, and using DGA solution of 65 wt%. Typical requirements at the above conditions for one MM scfd of feed gas are given below.

Steam, lb/MM scfd	17,000
Cooling water, gal/MM scfd	None Required

In a commercial Econamine plant, the solvent loss rate is estimated to be about 0.35 gal/MM scf of feed gas.

Environmental Considerations

A small amount of stable degradation products may form. The final disposition of amine sludges must be determined for each installation. In coal conversion plants, amine sludges will probably be mixed with solid waste or ash.

Remarks

The Econamine process effectively removes H_2S to less than 4 ppm in the feed gas. The new variations of the design parameters developed by Fluor Corporation should offer more environmentally acceptable benefits than the conventional Econamine process in terms of reduction in energy consumption and improved hydrocarbon recovery.

References

1. Bucklin, R. W. et. al., 'GPA Explores H_2S Removal Methods," Oil and Gas Journal, Vol. 76, No. 29, July 17, 1978, pp. 66-73.

2. Tennyson, R. N., et. al., "Process Improves Acid Gas Removal, Trims Costs, and Reduces Effluents," Oil and Gas Journal, August 23, 1976, pp. 130-132.

3. "Gas Processing Handbook," Hydrocarbon Processing, April 1979, p. 11.

4. Holder, H. L., "Diglycolamine - A Promising New Acid -Gas Remover," Oil and Gas Journal, Vol. 64, No. 18, 1966, pp. 83-86.

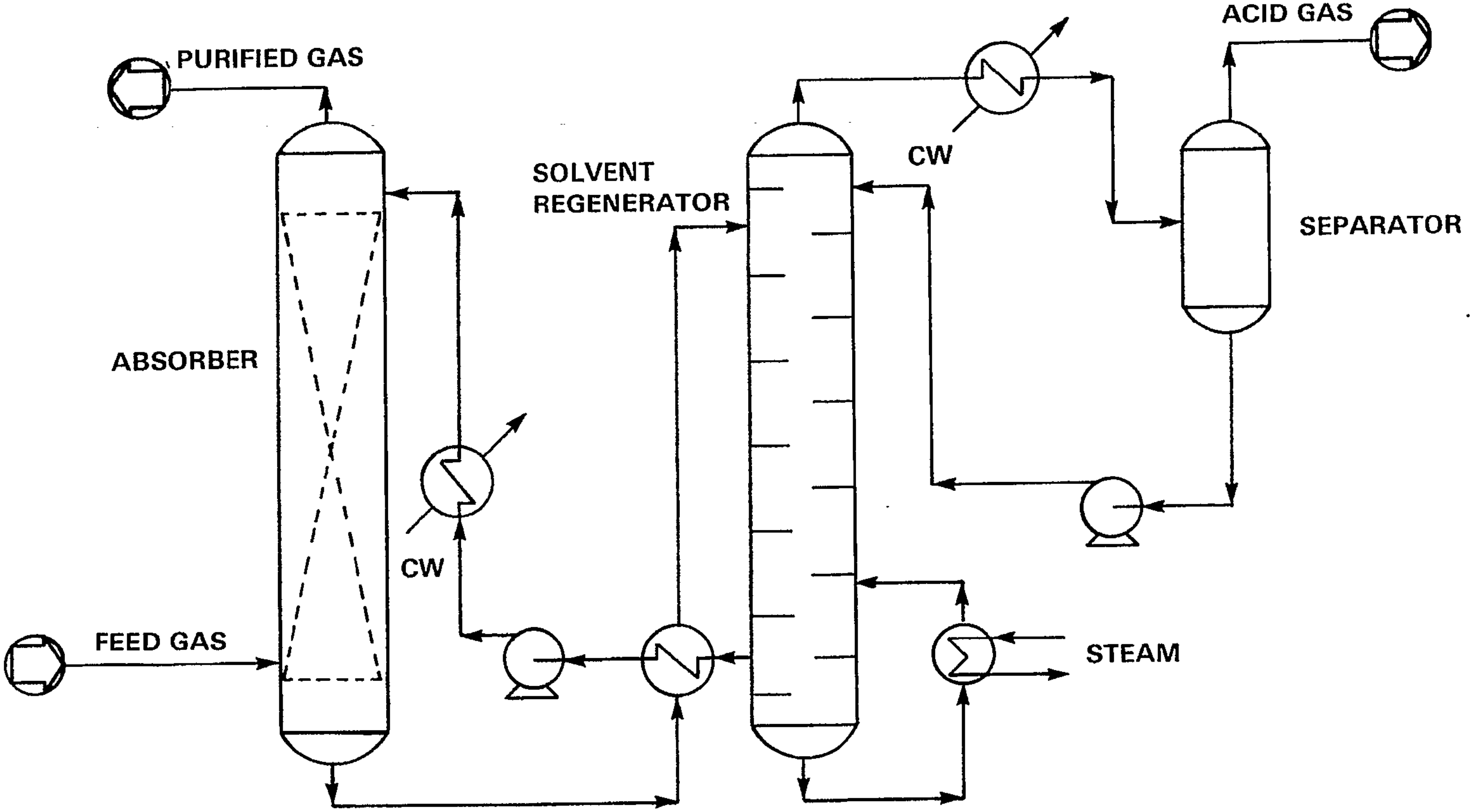

Figure 3A.10-1 Fluor Economine Process.

3A.11 FLUOR SOLVENT

Licensor

Fluor Engineers and Constructors, Inc.
Irvine, California

State of Development[1]

The application of propylene carbonate as a physical absorbent for acid gas removal was developed by the Fluor Corporation.

A total of 9 plants - 5 on natural gas, 1 in hydrogen production, and 3 in ammonia production - use the propylene carbonate absorption process.

Process Description[1] [2]

A typical process is shown schematically in Fig. 3A.11-1. Sour feed gas enters the bottom of the absorber, and the lean solvent is pumped to the top of the absorber at or below ambient temperature The rich solution leaves the bottom at a slightly higher temperature because of the heat of absorption of the acid gases. In addition to CO_2, H_2S, and other organic sulfurs, a small quantity of hydrocarbons and water vapor is also dissolved in the solvent. Then the spent solution from the absorber goes through several stages of flashing to disengage the absorbed gases and regenerate the solvent.

The first-stage flash is operated at a high pressure. A major portion of the dissolved hydrocarbons is released in the first-stage flash. The liquid from the first flash undergoes a second-stage flash to a lower pressure. The second-stage flash gas may be used to drive an expander turbine to recover power during expansion. The third-stage flash of solvent operates at atmospheric pressure. In this last stage, most of the dissolved acid gases in the solvent are released except the acid gases that remain in solution because of the equilibrium conditions. The regenerated lean solvent is recycled back to the top of the absorber. The regeneration level of the lean solution can be further lowered to a desired concentration, if necessary, with the addition of gas or air stripping or vacuum flashing of the solution. Power is normally recovered by use of hydraulic turbines between flashes.

Chemical Description[3]

The Fluor solvent process uses propylene carbonate ($C_3H_6CO_3$) for physical absorption of H_2S, CO_2, and other organic sulfur pounds in the sour gas. No chemical reaction is involved. Acid gases loading of the physical solvent is proportional to the partial pressure of acid gases in the feed stream. The process is reversible: when the pressure is reduced, the desorption of acid gases occurs. During desorption, the absorbed acid gases are released according to solubility limitations of each component in various flashing stages. The solubility of acid gases in propylene carbonate favors high pressure and low temperature operation. The refrigeration effect of solvent flash often is sufficient to make the absorber operate below the ambient temperature without refrigeration and will reduce the recirculation rate of the solvent.

Operating Limits

The physical absorption process favors high-pressure operation. Many plants are currently operating at feed gas pressure of 850-1000 psig. Economics will be less favorable for low-pressure gas.

Purification Limits

The process may reduce the H_2S level to less than 4 ppmv and the CO_2 level to less than 0.3%V. The exact amount of acid gas removal will depend upon the process conditions. Propylene carbonate also absorbs water moisture. Product gas will almost always meet pipeline specifications for water. However, drying of feed gas may be necessary to prevent water buildup in the solvent and hydrate formation.

Utility Requirements

Cooling water - little or none.
Electricity - function of acid gas content; normally low.

Environmental Considerations

H_2S exiting the atmospheric flash drum requires processing in a sulfur recovery unit, such as a Claus unit.

Remarks

The Fluor Solvent process employs propylene carbonate to absorb acid gases by physical absorption. Desorption of acid gases is carried out by reducing solvent pressure in several stages. For high-purity treated gas, vacuum flashing or stripping will be required after atmospheric flash.

The solvent is not considered corrosive. Carbon steel is a suitable material of construction for all equipment and piping in this process.

Fluor claims that this process is lower in capital and operating costs than other physical absorption processes.

References

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2. Riesenfeld, F.C. and Kohl, A.L., "Gas Purification," Gulf Publishing Co., 1974, pp. 717-725.
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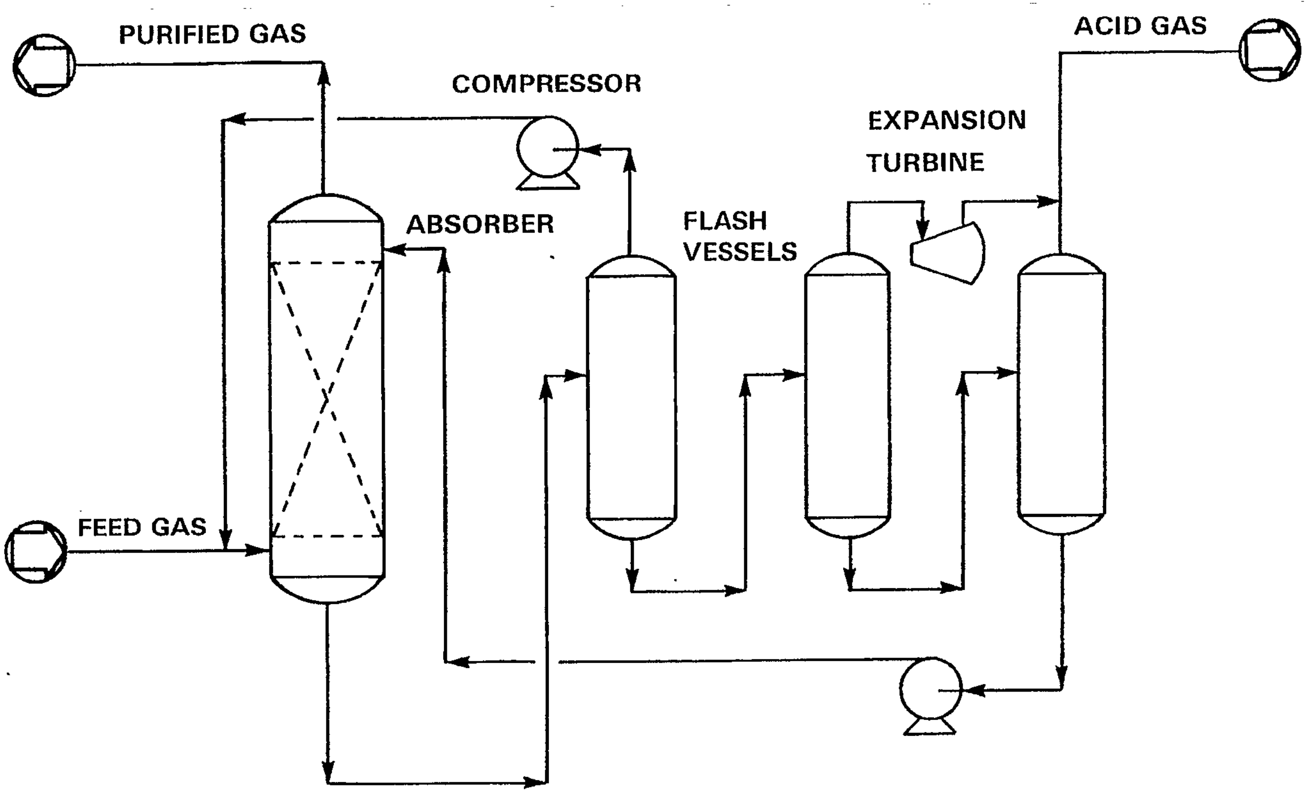

Figure 3A.11-1 Fluor Solvent Process.

3A.12 IRON OXIDE (IRON SPONGE)

Suppliers

1. Perry Gas Processors, Inc.
   P. O. Box 7059
   Odessa, TX 79760

2. Varec Division
   Emerson Electric
   11842 Monarch St.
   Garden Grove, CA 92641

State of Development[1]

The iron oxide gas-purification process for the removal of sulfur compounds from industrial gases was first introduced in England in the 1860s. It is still used on a large scale for the treatment of coal gases, although more recently developed wet purification processes are gradually replacing it. The process is well suited for sweetening small volumes of gas having low H_2S content.

Process Description[2] [3] [pc]

A simplified flow diagram of the basic iron oxide purification process is shown in Figure 3A.12-1. Feed gas containing H_2S is passed through a bed of hydrated ferric oxide, where H_2S is adsorbed. Upon exposure to atmospheric oxygen, the ferric sulfide is oxidized, yielding elemental sulfur and ferric oxide; the latter is then ready for the next sulfur adsorption cycle.

This cycle can be repeated a number of times until the surface area of the iron oxide particles becomes so covered with elemental sulfur that a loss of activity and an excessive pressure drop result. When the oxide is completely loaded, it is removed from the chamber and replaced with fresh oxide. Spent adsorbent is usually discarded, but the sulfur can be recovered if it is economically attractive to do so. In some instances, it is burned to form SO_2, which is then used in sulfuric acid manufacture. Other processes are available for elemental sulfur recovery by solvent extraction.

Iron oxides used for gas-purifying materials are classified as either unmixed or mixed oxides. Unmixed oxides are prepared from iron ore or metallic iron and contain approximately 75% ferric oxide, 10% water, and 15% impurities. Other sources of unmixed oxides are bauxite purification residue, which contains 25 to 50% ferric oxide, and natural bog ores, which consist of hydrated ferric oxide mixed with fibrous and peaty material containing about 45% water.

Mixed oxides are prepared by supporting finely divided ferric oxide on materials of large surface area and loose texture, such as wood shavings or granulated slag. These materials serve as inexpensive carriers for the ferric oxide powder. When wood shavings are used, the process is generally referred to as the "iron sponge" process.

Mixed oxides, as compared to unmixed oxides, have the advantage that their bulk density, iron oxide content, moisture content, and pH can be controlled more accurately. They have less tendency to coke, and higher sulfur loadings can be achieved with them.

The oxide vessel types include conventional box, deep box, tower, and tower box purifiers. Regeneration may be accomplished by exposure of the oxide to atmospheric oxygen after discharge from the bed. More commonly, a small amount of air is introduced continuously into the feed gas so that H_2S adsorption and oxide regeneration take place in the bed simultaneously. Alternatively, as shown in Figure 3A.12-1, the oxide can be regenerated on an intermittent basis, using by recirculating gas containing a small amount of air. In this method, two or more beds are used so that one bed can be regenerated while the other is in use. While a bed of iron oxide is in use, the moisture content and pH in the bed should be controlled to maintain the adsorption reaction.

Design of an iron sponge treating vessel should be based both on linear velocities through the bed and on contact time. Once these parameters are determined, it is necessary to determine if the bed life will be satisfactory.

The superficial linear velocity through the bed should not exceed 10 ft per minute, based on the empty vessel cross sectional area and the gas volume corrected to ACFM at flowing temperature and pressure. Pressure drop through the bed should be approximately 1 - 2 psi per foot of bed depth.

The sponge bed should be of sufficient size to allow a maximum space velocity of 60 actual cubic feet per hour per cubic foot of bed for each grain of H_2S in the inlet gas. In a typical sponge treating unit, the gas channels to some extent along the shell of the vessel. The H_2S front moves through the bed as an inverted cone, and the greater the linear and space velocities, the steeper will be this cone. Thus, if too high linear and space velocities are used, there will be a large mass of unreacted sponge in the center when the H_2S breaks through around the vessel shell.

Chemical Description

The adsorption of H_2S on ferric oxide bed takes place according to the following reaction

$$Fe_2O_3 + 3H_2S \longrightarrow Fe_2S_3 + 3H_2O$$

The bed is regenerated according to the following reaction

$$2Fe_2S_3 + 3O_2 \longrightarrow 2Fe_2O_3 + 6S$$

Operability Limits[3]

Earlier iron oxide purification plants were operated at near atmospheric pressure. In recent years, several plants ranging in capacity from 6 to 20 MM scfd are operating at pressures of 100 to 325 psig. One high-pressure plant treats 7 MM scfd at 1000 psig. Operating temperatures in the range of 80 to 120°F appear to be common. Temperatures above this range result in decreased removal efficiency.

Gases containing as much as 1000 grains H_2S/100 scf (1.6 vol%) are treated in European plants, with a total sulfur production of 8 to 10 tpd. At this level of H_2S concentration, however, the iron oxide life would be so short that the process economics are questionable. More recent installations of the iron oxide process are limited to gases having H_2S concentrations in the range of 10 to 75 grains of H_2S/100 scf of gas (160 to 1200 ppm).

Purification Limits

The iron oxide process is capable of reducing the H_2S concentration in a feed gas to a very low level. In one commercial natural gas application, the H_2S concentration was reduced from 7 grains/100 scf (112 ppm) to 0.22 grains/100 scf (4 ppm), and the mercaptan sulfur content was reduced from 1.3 grains/100 scf to 0.15 grains/100 scf.3 A combination of an iron sponge bed to remove H_2S and an activated carbon bed to remove organic sulfur lowers the total sulfur content even further. Hydrogen cyanide, if present, is also removed by the iron oxide process, but CO_2 is not.

Utility Requirements

The utility requirements for the iron oxide process are small. Electric power is required to operate the air blower for oxide regeneration, and small amounts of water or steam are required to keep the bed moist during operation.

Environmental Considerations

Spent iron oxide or iron sponge is usually discarded and covered with soil to render it inert.

Remarks

The iron oxide bed can be regenerated repeatedly before it becomes fully loaded with sulfur. The process can reduce the H_2S content of the feed gas to ppm level. The beds fully loaded with sulfur must be disposed of, and therefore the process is normally used for sulfur removal only on a small scale.

References

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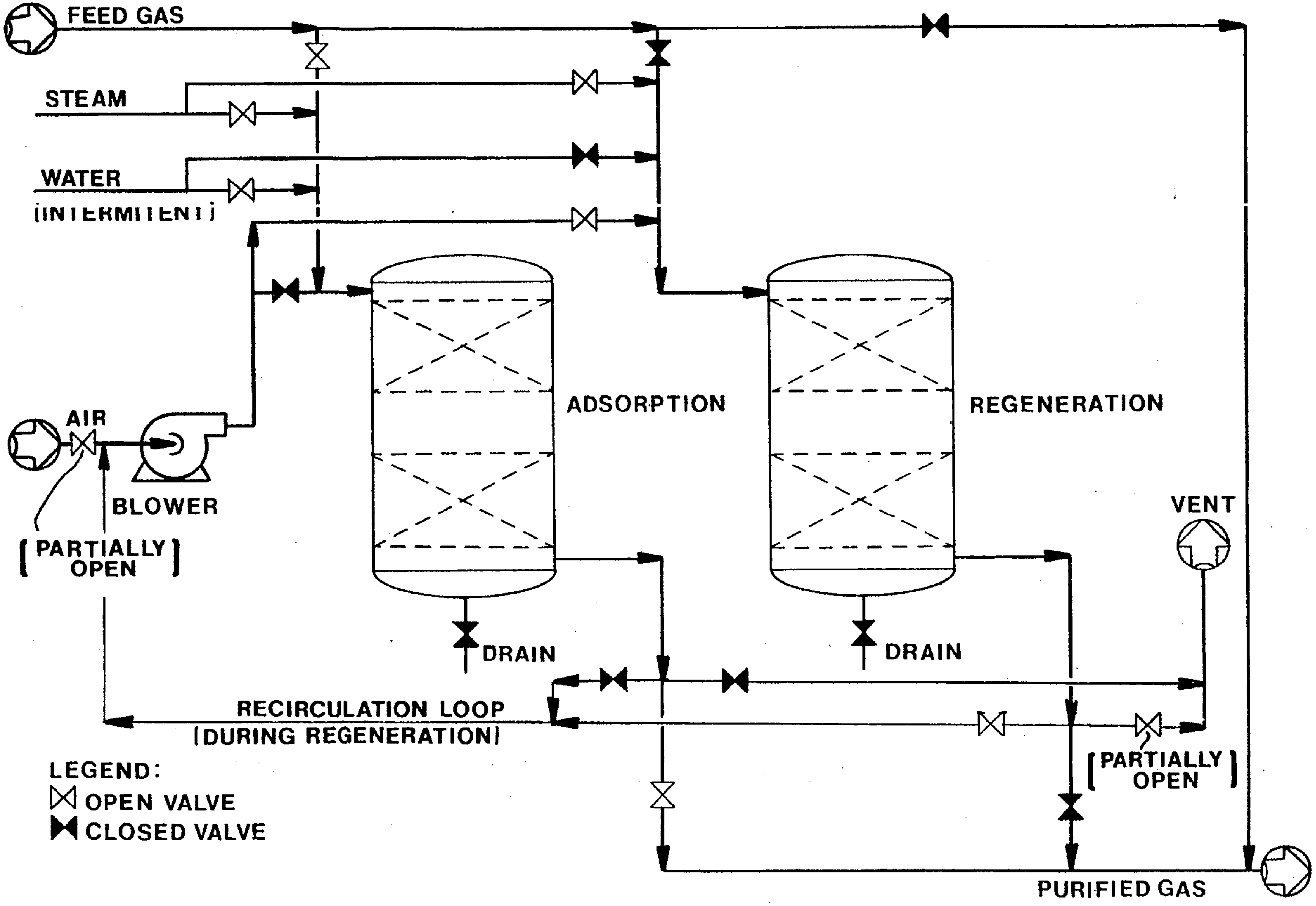

Figure 3A.12-1 Iron Oxide (Iron Sponge) Process.

3A.13 MEA

Licensor

Virtually all engineering companies in the gas purification field offer this generic process.

State of Development[1] [2]

Alkanolamines are widely used to absorb acid gases (CO_2 and H_2S) from sour feed gas. In particular, mono-ethanolamine (MEA) has been used for many years to remove low concentrations of H_2S and CO_2 from natural and synthesis gases. The process has been improved by the incorporation of an amine guard corrosion inhibitor, developed by the Union Carbide Company, in the MEA solution.

Process Description[3] [4]

A schematic flow diagram is shown in Figure 3A.13-1. Sour gas containing CO_2 and H_2S is contacted countercurrently with MEA solution in a trayed or packed tower. Rich amine solution from the bottom of the absorber is preheated by heat exchange with hot lean solution from the bottom of the regenerator and is then flashed at reduced pressure in the regenerator. The rich solution is regenerated by steam stripping. The acid gases released from the solution by the steam go to the condenser at the overhead of the regenerator, where hydrocarbons and the solvent vapor are recovered. The solvent is recycled. Lean solution from the bottom of the regenerator is cooled by heat exchange with the rich solution. Further cooling is provided by an air or water cooler. After cooling, the lean solution is pumped back to the top of the absorber. Purified gas from the overhead of the absorber is passed through a condenser to recover solvent from the purified gas.

Chemical Description[1]

The principal chemical reactions occurring when MEA solution is used to absorb CO_2 and H_2S are as follows:

$$RNH_2 + H_2S \longleftrightarrow RNH_3 \bullet HS$$

$$RNH_2 + CO_2 + H_2O \longleftrightarrow RNH_3 \bullet HCO_3$$

or

$$2\ RNH_2 + CO_2 \longleftrightarrow RNH\ CO_2 \bullet NH_3R$$

R denotes the ethanol group; i.e. (C_2H_4OH)

MEA is a strong base and reacts rapidly and non-selectively with acid gases. Because of its lower molecular weight, it can remove more acid gases than other amines on a unit weight or volume basis. This reduces the amount of recirculation necessary to remove a given amount of acid gases.

MEA reacts irreversibly with carbonyl sulfide and carbon disulfide. This results in buildup of solids in the MEA solution and may increase solution losses. Reclamation of the reaction products by caustic solution releases amine from the degraded sulfur compounds.

High vapor pressure, corrosion, and foaming tendency are the problems usually encountered in MEA process. These are minimized by the use of an amine guard corrosion inhibitor.

Operation Limits[2] [4]

The absorber operates at a temperature range of 110-160 °F, depending on the cooling medium available and acid gas loading of the rich solution. The regenerator operating temperature range is about 205-250 °F. When amine guard inhibitor is used in MEA solution, live steam can be injected directly at the bottom of the regenerator, which operates at a temperature slightly higher than 250 °F. The process is not sensitive to pressure, and tne regenerator operates at only a few pounds above atmospheric pressure to facilitate desorption.

Purification Limits[1]

MEA can reduce H_2S content in the purified gas to less than 1 ppm and CO_2 to less than 0.1% by volume.

Utility Requirements

The utilities for a MEA process will depend upon the MEA circulation rate and the concentrations of the acid gases in the circulated solution.

Environmental Considerations[4]

The MEA process is a non-selective chemical absorption process. The rich MEA solution from the absorber is composed primarily of absorbed gases: CO_2, H_2S, organic sulfur, and hydrocarbons. The concentrations and amounts of each of these components will depend upon the feed gas composition and the operating conditions. The vapor from the regeneration tower will require further treatment to control emissions of sulfur compounds and hydrocarbons.

Remarks

MEA is one of the well-known alkanolamines processes. The process removes CO_2 and H_2S non-selectively from sour gases. Sufficient data are available for design of acid gas removal systems for different feed gas compositions. The development of the proprietary amine guard inhibitor makes the MEA Process attractive because it reduces energy consumption and corrosion in the system.

References

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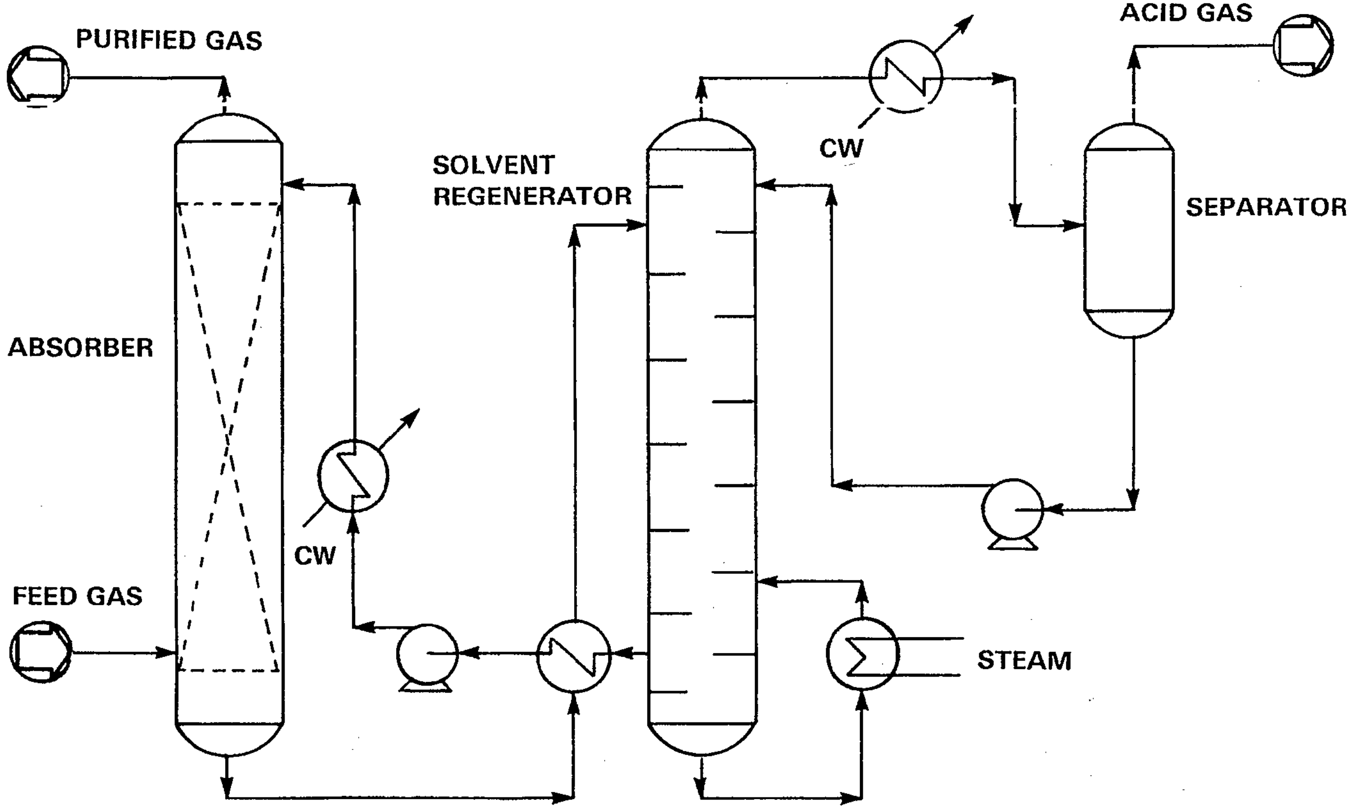

Figure 3A.13-1 MEA Process.

3A.14 MDEA

Licensor

The Dow Chemical Company
Patent Department
Freeport, TX 77541

State of Development[1] pc

The process uses an aqueous solution of methyl-di-ethanol-amine (MDEA) to remove H_2S by chemical absorption from industrial gases. In the United States, early pilot plant operations were carried out by Fluor Corporation, beginning in the late 1940s. Currently developmental work is being done by several companies, including Dow, Shell, Union Carbide, Phillips, and Exxon. Pilot plant operations and a commercial scale test of 20 weeks duration showed MDEA to have a higher selectivity toward H_2S in the presence of CO_2 than do other primary or secondary amines, such as MEA or DEA.

It is estimated that at least twenty MDEA units are operating in the U.S and several in Europe. The upgrading of the H_2S content of Claus sulfur-plant tail gas and treating of natural gas for H_2S removal to pipeline specifications are the known areas of application. The process is also being selected for some CO_2 removal applications because it can offer some energy savings over other amines.

Process Description[2] [3]

The MDEA process is shown schematically in Figure 3A.14-1. The sour feed gas enters the bottom of the absorber, and an aqueous solution of MDEA (usually 30-50 wt%) is pumped to the top. This lean solution absorbs most of the H_2S and some of the CO_2 as it passes countercurrently to the gas. The purified gas exits at the absorber top.

Rich solution containing absorbed acid gases is heated by interchange with the hot lean solution and flows to the stripper for MDEA regeneration. Here the absorption reactions are reversed by stripping steam generated in the reboiler. As the steam passes countercurrently to the rich solution, regenerated acid gases are driven overhead. Steam is then condensed, separated from the acid gases, and refluxed to the stripper, while the acid gases go to sulfur recovery.

A portion of hot lean solution maybe withdrawn from the stripper bottom and fed to a redistillation unit, if necessary. Here the spent amines, degraded by reactions with HCN and organic acids, are recovered by distillation at higher temperatures. Unrecovered amines form a sludge, which is pumped to a settling tank and sent to disposal. Recovered amines and makeup solution pass overhead from the redistillation unit and return to the stripper. The need for redistillation unit would have to be determined on a case-by-case basis.

The hot lean solution is pumped from the stripper bottom and cooled by interchange with the cool rich solution. It is then further cooled in a water cooled or air cooled exchanger and returned to the absorber.

Chemical Description

H_2S, HCN, organic acids, and a portion of the CO_2 are chemically absorbed from the gas in a 30-50 wt% aqueous solution of methyl-di-ethanol-amine $((HOC_2H_4)_2NCH_3)$. Normal absorption reactions proceed as follows (MDEA is represented as R_2NCH_3):[2]

$$R_2NCH_3 + H_2S \longleftrightarrow R_2NHCH_3 \bullet HS$$
$$R_2NCH_3 + CO_2 + H_2O \longleftrightarrow R_2NHCH_3 \bullet HCO_3$$

The acid gases are absorbed in the absorber, and when heat is applied in the stripper, these reactions are reversed, freeing the acid gas. Reactions between MDEA and HCN are reversible in oxygen-free operation. However, in the presence of oxygen and H_2S, HCN forms SCN. The reaction of SCN and MDEA is not reversible. Although MDEA is selective toward H_2S in the presence of CO_2, the selectivity decreases as the degree of H_2S removal increases.

Performance of MDEA has been compared with that of tri-ethanol-amine (TEA) because both are tertiary amines and are selective toward H_2S. It is reported that MDEA is more stable and more reactive than TEA and also has a slightly higher loading capacity.

In the commercial scale test, some indication of foaming was encountered, particularly in the still. This was overcome by the addition of a commercial foam inhibitor. The use of silicone antifoam agents has been successful in the control of foam.

Operability Limits

The heats of reaction and possible degradation of MDEA at higher temperatures limit the operating temperatures. The absorber usually operates at 80-125 °F, the stripper at 240-250 °F, and the redistillation unit, if used, at 250-300 °F. The feed gas should be at 60-120 °F to maintain the reactions and operating temperature limits. The absorber will operate over a wide range of feed gas pressure, 0-1000 psig. The stripper usually operates at lower pressures, 7-10 psig. The redistillation unit, if used, is operated in vacuum. The process can be adapted for various feed gas compositions and rates and outlet gas concentrations by selecting proper operating conditions. The process absorbs hydrocarbons (C_3+) to a lesser extent than DGA, DIPA, and MEA. It is comparable to DEA in hydrocarbon absorption.

Purification Limits

Pilot-plant operations and commercial scale tests show that the H_2S content in the purified gas can be reduced to less than 4 ppm even at low pressures. Over 99% of the H_2S can be absorbed, with CO_2 being removed to a lesser extent. The exact amounts of H_2S, CO_2, and other acid gases removed depend upon the actual operating conditions. This process does not remove mercaptans.[4]

Utility Requirements

Typical utility requirements per MM scf of feed gas at 105 °F and 60 psig, containing about 0.6% H_2S and 10% CO_2, which are reduced to 50 ppm H_2S and 3.3% CO_2 in the purified gas, are estimated to be

Steam, lb/MM scf	14,000
Cooling Water, gal/MM scf	Not Available
Electric Power, kWh/MM scf	15
Solvent Loss, lb/MM scf	0.5

With 965 ppm H_2S and 7.3% CO_2 in the purified gas, the requirements are

Steam, lb/MM scf	6,600
Cooling Water, gal/MM scf	Not Available
Electric Power, kWh/MM scf	8
Solvent Loss, lb/MM scf	0.5

Environmental Considerations

The acid gas exiting the stripper requires further processing in a sulfur recovery unit, such as a Claus or Stretford. Final disposition of amine sludges generated in the process must be determined for each installation. In coal conversion plants, they are generally mixed with waste ash.

Remarks

The MDEA process has lower heats of reaction for both CO_2 and H_2S than do most of the amines in this service. This property, coupled with the absorption of only 30-65% of the inlet CO_2, may offer some energy savings, and, in spite of the solvent's costing two to three times as much, the MDEA process could be lower in costs for a given installation than other amine processes. Also, with the stricter EPA air quality standards of today, selective H_2S absorption, as offered by MDEA, may be desired in certain applications to obtain a high H_2S concentration in the Claus plant feed. It is also expected that the cost of MDEA production will decrease if the process is widely accepted commercially. MDEA is oxidatively more stable than the other amines.

The MDEA process, although it does not contain all the desirable characteristics of an ideal selective H_2S solvent, does have a good overall balance of worthwhile properties. The low utilities coupled with favorable selectivity and capacity makes the process worthy of serious evaluation when searching for a versatile acid gas removal process.[2]

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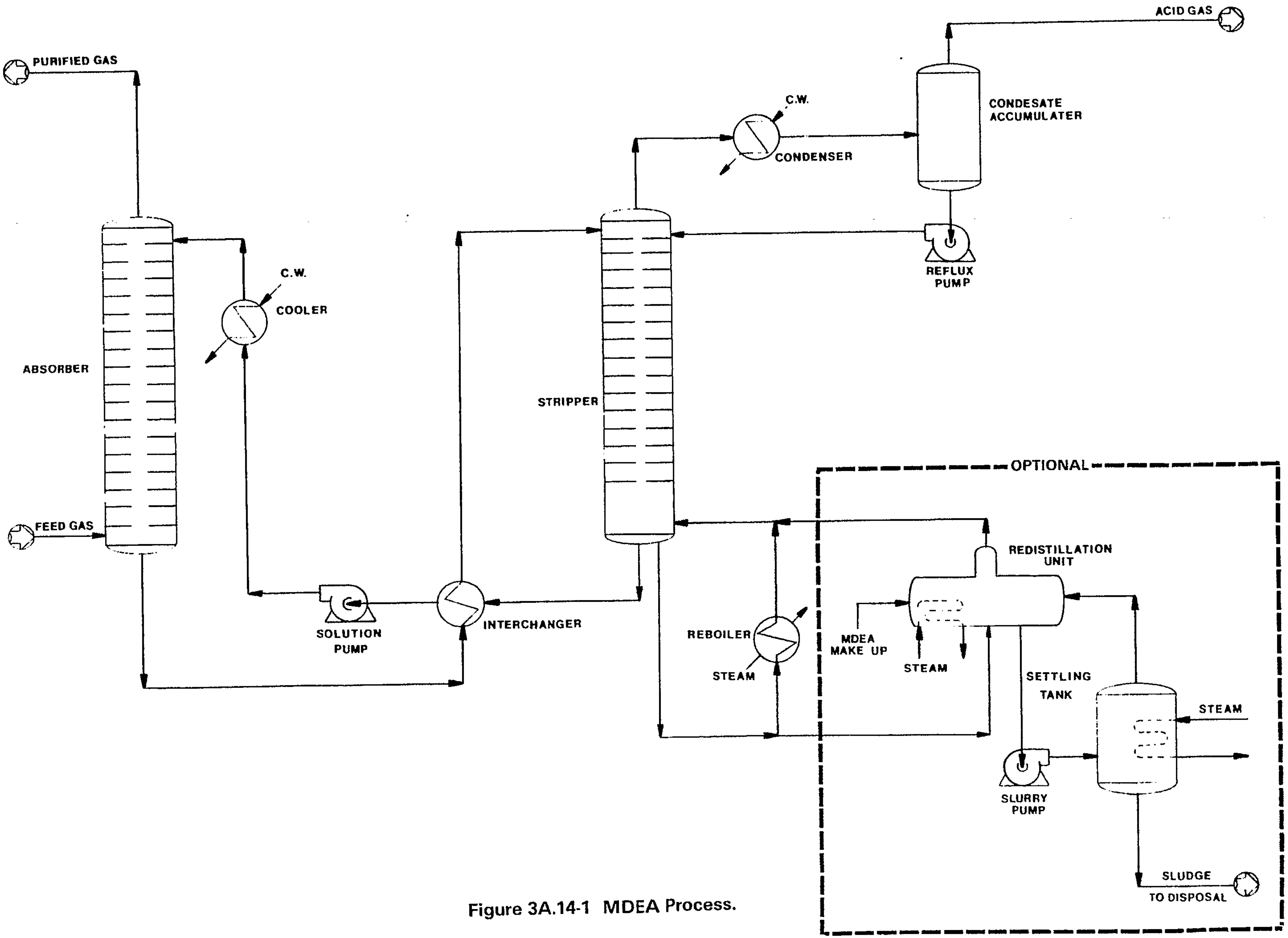

Figure 3A.14-1 MDEA Process.

3A.15 MOLECULAR SIEVE

Supplier

Union Carbide Corporation
Linde Molecular Sieve Department
Old Saw Mill River Road & Route 1006
Tarrytown, NY 10591

State of Development

Molecular sieves belong to a class of compounds known as zeolites. Naturally occurring zeolites that release water when heated and reabsorb it when cooled were first noted two centuries ago. In 1948, Union Carbide Corporation started to investigate adsorption as a possible method for separation of gases, using various adsorbents including natural zeolites. This investigation led to the preparation and production of synthetic zeolites, or molecular sieves. Synthetic zeolites have structures different from those occurring in nature.

Development of the gas adsorption process using molecular sieves has been extensive. Commercially successful molecular sieve adsorption processes are currently marketed for a variety of applications in the natural gas, petroleum, and petrochemical industries. Well over 150 commercial desulfurization units have been installed, both in the U.S. and abroad.[1] Gas flow rates range from 1 to over 1000 MM scfd.

Process Description[2]

A flow diagram for a typical molecular sieve drying/desulfurization process is shown in Figure 3A.15-1. The operation of this process is relatively simple. Gas to be dried and purified flows through the bed of molecular sieves at ambient temperatures of 60 to 120°F, and the sulfur compounds (H_2S, COS, mercaptans, etc.) and other impurities in the gas are adsorbed by the molecular sieves. The process is continued until the bed becomes saturated with adsorbed materials.

Regeneration of the bed involves passing a heated (550°F), dry, sweet, product-quality gas through the bed in a direction opposite to that used during adsorption. The source of the regeneration gas is usually a slip stream of purified gas leaving the bed in its adsorption cycle. After regeneration is concluded, the bed is cooled to operating temperature (85°F to 120°F) with a purified gas.

The operating scheme and number of beds are dictated by the gas feed rate and the concentration of impurities. Figure 3A.15-1 shows a two-bed operation with one bed on adsorption and the other on regeneration and cooling. This arrangement is practical when the sulfur content of the feed gas is low. Long cycle times can be justified, and therefore sufficient time is available to heat and cool one bed while the other is on adsorption.

When the feed sulfur content is relatively high, a three-bed operation, with one bed on adsorption, the second on heating, and the third on cooling, is desirable so that short cycle times can be achieved.

If the quantity of molecular sieve adsorbent required for a chosen cycle time is very large, a multiple bed operation becomes practical. For example, a four-bed system may be used, in which two beds are on adsorption in parallel while the third bed is being heated and the fourth is cooling.

Chemical Description

Molecular sieve processes are physical adsorption processes.

Operability Limits

The ranges of operating conditions for commercial natural gas sweetening have been reported as follows[1]

Feed Rate, MM scfd	1 to over 1000
Pressure, psig	200 to 1200
Adsorption Temperature, °F	60 to 120
H_2S Content, grains/100 scf	0.5 to 600 (8 ppm to 1 vol%)
H_2O Content, lb/MM scf	1 to 60
CO_2 Content, vol%	1 to 50
Acid Gas Ratio (mole CO_2:mole H_2S)	30 to 1050

Gas purification could be carried out at pressures lower or higher than those shown above.

Adsorbents exhibit lower capacities with increasing temperature. In the ambient temperature range, the loading differential resulting from a 10°F change in feed temperature can cause a difference of as much as 20% in molecular sieve requirement. This necessitates accurate prediction of feed temperature, taking into account any extreme climatic conditions.

Molecular sieves are produced in a range of pore diameters, and the proper sieve size must be used for each application. In natural gas desulfurizing, molecular sieves with a nominal pore diameter of about 5 angstroms or larger are generally used.

Purification Limits[1]

Sour natural gas can be desulfurized to below 1/4 grain H_2S/100 scf (4 ppm). Molecular sieve processing can also be made selective for removing H_2S and other sulfur compounds in the presence of CO_2.

Molecular sieves having the proper pore size to remove sulfur compounds will preferentially remove H_2O, so the gas leaving is completely dry. This could be a disadvantage in the case of a water-saturated gas from a coal conversion process if water removal is not required, since a larger sieve bed would be necessary.

Utility Requirements

Meaningful utility requirements for molecular sieve processes are not readily available because operating conditions vary widely, particularly with respect to methods for handling the regeneration gas requirement. The main energy usage is in heating the regeneration gas.

The normal life expectancy of a fresh charge of molecular sieve adsorbent ranges from 2 to 3 years.[3]

Environmental Considerations

The sulfur compounds adsorbed in the molecular sieve bed are ultimately desorbed when the bed is regenerated and appear in the regeneration gas stream. The concentration of sulfur compounds in the regenerated gas is high, since the volume is low. The regeneration gas stream may be used as fuel gas, in which case the sulfur would be converted to SO_2 and discharged to the atmosphere. If this discharge exceeds the permissible level of SO_2 discharge for the entire plant, the regeneration gas will require further treatment to remove the sulfur compounds.

Remarks

Molecular sieves are highly selective adsorbents. Impurities in a certain molecular diameter range are removed, depending on the selected nominal pore size of the molecular sieves. The sieves are regenerable and remove sulfur compounds down to ppm levels. Since they adsorb compounds on the basis of their molecular diameter, compounds other than the impurities may also be adsorbed.

References

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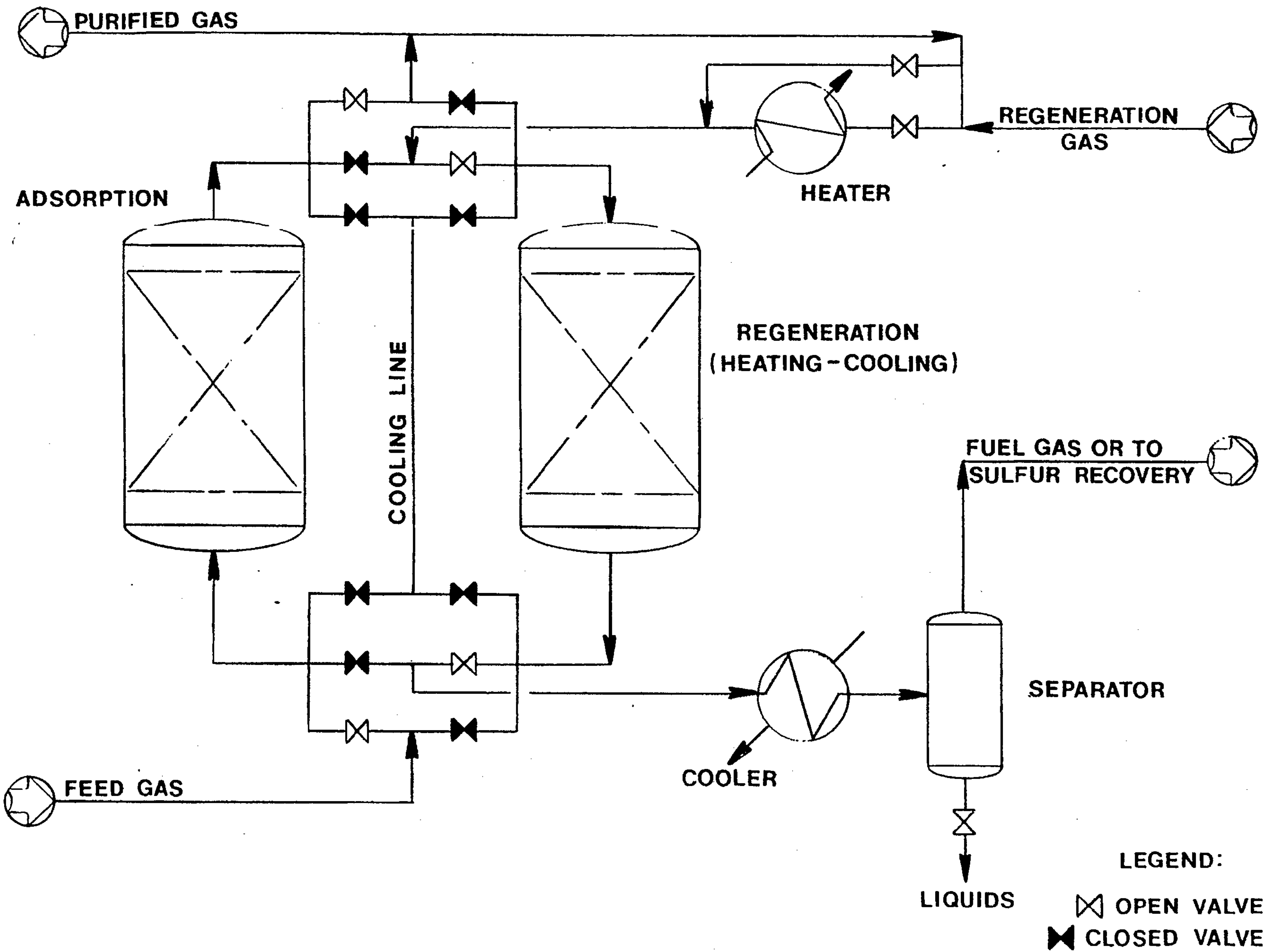

Figure 3A.15-1 Molecular Sieve Process For Sulfur Removal From Fuel Gases.

3A.16 PURISOL

Licensor

Lurgi Kohle und Mineraloeltechnik GmbH
Bockenheimer Landstrasse 42
Postfach 119181, D-6000
Frankfurt Am Main 1
West Germany

State of Development

The Purisol process was developed by Lurgi Mineraloetechnik GmbH. in West Germany for removal of acid gases from natural gas, hydrogen, and synthesis gas by physical absorption in N-Methyl-2-Pyrolidone (NMP or M-Pyrol). Typically, the process is used for (1) reduction of high CO_2 concentrations to a low level, (2) bulk removal of acidic components to a moderate level with a simplified flash regenerator system, and (3) selective H_2S removal. Five plants are in operation, processing a total of 437 MM scfd of feed gas; two are used in high-pressure hydrogen manufacturing processes, and three are used for treating natural gas. A plant with a 17 MM scfd throughput is under construction.[1] [pc]

Process Description[2]

The Purisol process is shown schematically in Figure 3A.16-1. Sour feed gas enters the absorber, where it is first dehydrated with a slip stream of rich NMP and then scrubbed with regenerated NMP. The NMP physically absorbs H_2S, CO_2, and some of the hydrocarbons as it flows countercurrently to the feed gas. Entrained NMP is recovered by a water wash before the treated gas exits from the top of the absorber. If the purified gas must be dry, a glycol system is used for NMP recovery.

Rich solvent is flashed at relatively high pressure in the lower section of the absorber. Co-absorbed hydrocarbons and part of the acid gas are separated, recompressed, cooled, and recycled to the feed gas. The rich solvent, still containing absorbed acid gases, is cooled and then regenerated in a stripping column by two-stage flashing to atmospheric pressure. The H_2S and part of the CO_2 are separated in the first flash and flow to the solvent dryer. Residual CO_2 is separated from NMP in the second stage by countercurrent stripping with air or nitogen. The lean solvent generated in this manner is then pumped to the absorber for reuse.

NMP/water mixtures from the absorber and stripper dehydration sections are combined and sent to the solvent dryer. Off-gas from the first stripper flash and wash water from the absorber also feed to the dryer, where water and acid gas are separated from the NMP by distillation. Water-saturated acid gas passes overhead to recovery, and dehydrated NMP returns to the stripper.

Chemical Description[3]

The Purisol process uses N-Methyl-2-Pyrolidone (NMP) for physical absorption of H_2S, CO_2, and other acid gases. Since NMP has a high solubility for H_2S and CO_2, chemical reactions are not required.

Since the absorption is physical, this solubility increases as the absorption pressure and the sour gas concentration increases. The absorption is easily reversed, and the H_2S and CO_2 are separated from the NMP simply by reduction of the pressure. The NMP warms as it absorbs H_2S and CO_2 and cools when they are flashed out; therefore a small amount of cooling, usually by cooling water, is customarily provided to offset frictional heat produced in the system.

Operability Limits[4]

The absorption and regeneration cycle usually operates at 80°-105°F. Higher or lower temperatures can be used, if necessary, to accommodate special conditions, such as available cooling water temperature. The absorber will operate over a wide pressure range, from low pressure to over 1000 psig, but the higher pressure favors the quantity and quality of absorption. The process can be modified through proper selection of pressure and temperature to meet a variety of feed gas and treated gas requirements.

Purification Limits[4]

The process typically reduces H_2S concentration to 4 ppm and CO_2 concentration to 2-3 vol%, but purified gas concentrations can be as low as 2 ppm H_2S and 10 ppm CO_2. The exact amount of removal depends upon whether the process is used for selective or bulk removal of H_2S or CO_2 and the actual process parameters selected.

Utility Requirements

Typical requirements per MM scf of a feed gas containing 6% H_2S and 15% CO_2 at 1070 psig, which are reduced to 2 ppm H_2S and 13.6% CO_2 in the purified gas

Steam, lb/MM scf	3,125
Cooling Water, gal/MM scf	13,300
Electric Power, kWh/MM scf	264
NMP Loss, lb/MMscf	2.1

Environmental Considerations

H_2S and other acid gases exiting the solvent dryer require further processing in a sulfur recovery unit, such as a Claus. Sulfur compounds in the vented stripping gas may or may not require further treatment, depending on the particular application.

Remarks

Purisol is a physical absorption process that offers high solubility (volume of acid gas/volume of solvent) at high acid gas partial pressures. Acid gas solubility is proportional to the acid gas partial pressure. Therefore, the Purisol process has an advantage over chemical solvents when treating high-pressure gases with high sour gas concentrations. The process may also be applied to small to medium H_2S concentrations in the feed gas if a selective and complete desulfurization is required.

Operating temperature, however, must be near ambient, and a certain minimum acid gas partial pressure is required, for the process to be run economically.

References

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2. Beavon, D. K., and Rosykowski, T. R., "Purisol Removes Carbon Dioxide from Hydrogen, Ammonia Syngas," Oil and Gas Journal, April 14, 1969, pp. 138-142.

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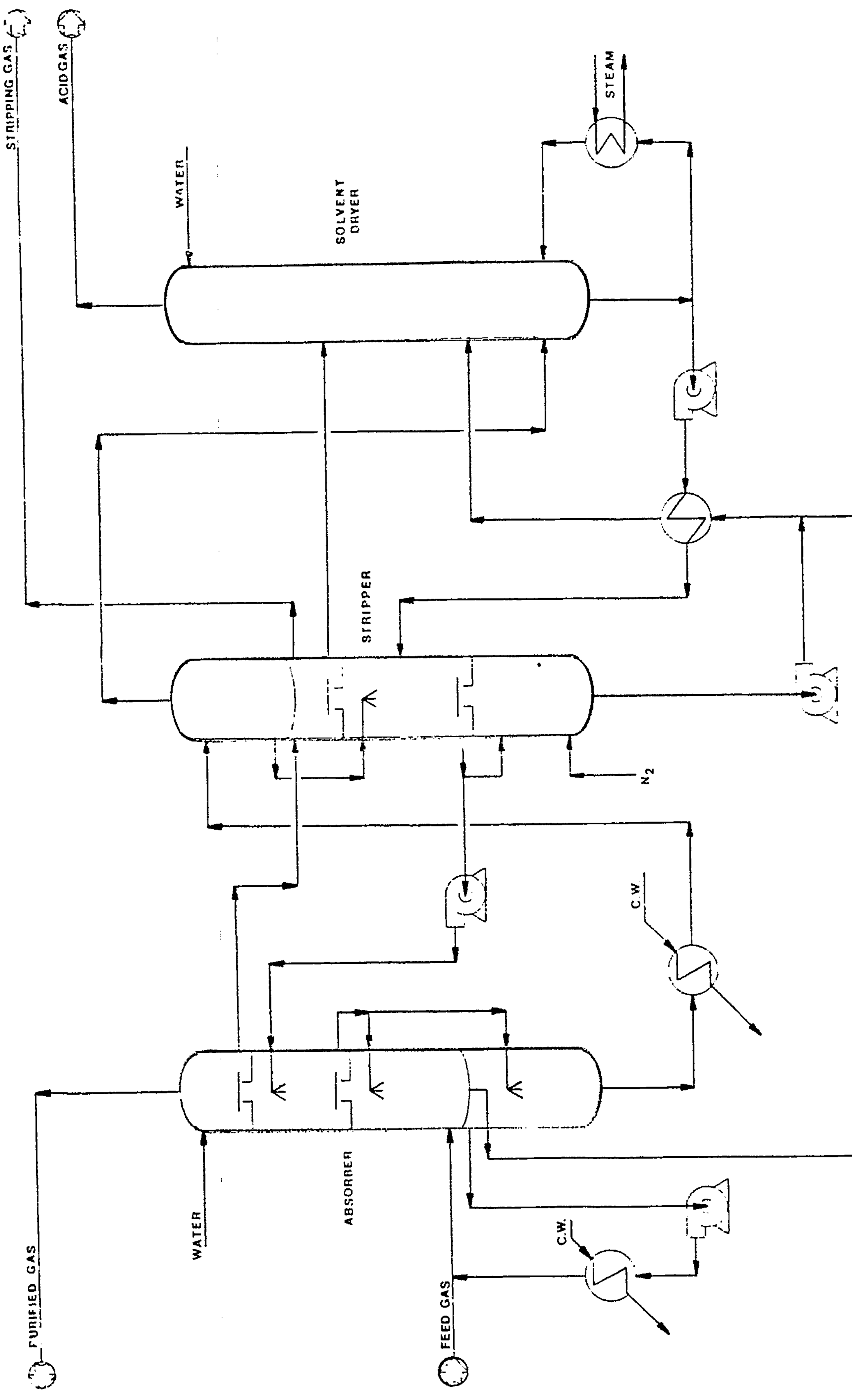

Figure 3A.16-1 Purisol Process.

3A.17 RECTISOL

Licensor

Lurgi Kohle und Mineraloeltechnik GmbH
Bockenheimer Landstrasse 42
Postfach 119181, D-6000
Frankfurt Am Main 1
West Germany

State of Development

The Rectisol process uses methanol (CH_3OH) for removal of acid gases by physical absorption at relatively low temperatures. The process is used for removal of H_2S, CO_2, HCN, NH_3, gum-forming hydrocarbons, higher hydrocarbons, and other impurities from coal or oil gasification processes that produce fuel gas, synthesis gas for ammonia, methanol, or SNG. It is also widely used in conjunction with low-temperature plants for hydrogen purification and separation of light hydrocarbons.

There are more than 37 Rectisol plants currently in operation and some additional plants under construction. Total capacity is over 6 billion scfd.[1 pc]

Process Description

Two schemes of the Rectisol process are frequently used in an ammonia synthesis or SNG plant.[2] The first scheme, the standard process, removes both H_2S and CO_2 simultaneously. The second scheme, the selective process, removes H_2S and CO_2 separately, in two stages in series. In synthesis gas production, the first stage is often arranged upstream of shift conversion, and the second stage downstream.

Figure 3A.17-1 shows a typical diagram for the two-stage Rectisol process following an oil gasification process. Four columns are used in the process: a first absorber to remove H_2S and COS, a first regenerator to strip the H_2S and COS, a second absorber to remove CO_2 after shift conversion, and a second regenerator to strip the CO_2. Feed gas is cooled by interchange with the outlet gas from the first absorber and by ammonia refrigerant and enters the first absorber at the bottom. Icing is prevented by injecting methanol into the gas stream prior to the cooling. Cool methanol from the high-pressure flash stage of the second regenerator is pumped to the top of the absorber. The CO_2-rich methanol physically absorbs H_2S, COS, and some CO_2 as it passes countercurrently to the feed gas. The absorber outlet gas, containing minimal amounts of H_2S and COS, is warmed by interchange with the feed gas and sent to shift conversion. Shifted gas is cooled by interchange with CO_2 separated in the second regenerator and purified gas. It is then cooled further by ammonia refrigerant and sent to the second absorber. Here, it is countercurrently contacted with methanol from the second generator to remove CO_2. Absorption of this large quantity of CO_2 produces heat, so the solvent warms up considerably during absorption, and then cools down during flash and strip regeneration. Ammonia refrigerant is also used to remove heat. Purified gas leaving the absorber is heated by interchange with the shifted gas before it leaves the plant.

Rich methanol from the first absorber, containing H_2S, COS, CO_2, and a small amount of hydrocarbons, is first flashed at an intermediate pressure to primarily disengage H_2, which is then recompressed and recycled to the absorber inlet. The flashed methanol is pumped to the first regenerator, where the acid gases are separated by heat provided by the regenerator reboiler. Sulfur-rich acid gases, containing H_2S, COS, and CO_2, exit the first regenerator top and go to sulfur recovery.

Lean methanol is pumped to the lower section of the second regenerator and mixed with stripped methanol of the second stage, and residual CO_2 is removed by stripping with nitrogen, yielding CO_2 and N_2 off-gases. Stripped methanol and the semi-stripped methanol from the middle of the second regenerator are pumped to the top of the second absorber for removal of CO_2 from the shifted gas. The CO_2-rich methanol is first flashed at a relatively high pressure to disengage the dissolved H_2 and CO, which are recompressed and recycled to the first absorber feed gas inlet.

Rich methanol then flows to the upper section of the second regenerator, where it is flashed to remove the remaining CO_2. Part of the lean methanol is pumped to the top of the first absorber. The remainder, together with the lean methanol from the first regenerator, is N_2-stripped in the lower section of the second regenerator.

For coal gasification applications, the Rectisol process has an added prewash system not shown here.

Chemical Description[3]

The Rectisol process is based on the principle that CO_2, H_2S, HCN, other organic sulfur compounds, benzene, and gum-forming hydrocarbons are highly soluble in polar solvent (usually methanol is used) at low temperatures and high pressures and are readily separated from the solvent when pressures are reduced. The solubility increases as the temperature decreases and pressure increases. The considerably higher solubility of H_2S compared with that of CO_2 allows selective removal of H_2S in the first absorber.

Operability Limits[3]

The process requires sustained operation at very low temperatures, and cooling must be supplied from an external refrigeration unit. Ammonia is frequently used as the refrigerant. This cooling is required especially in the second absorber, to remove process heat (incomplete heat exchange, cold losses, etc.). Insufficient cooling results in low absorption rates and an off-quality purified gas. Temperatures maintained are in the range of -100 to 0 °F in the absorbers, and up to approximately 150 °F in the regenerator with the steam reboiler. Higher-pressure operation favors this physical absorption process, so it is operated over a range of 300-2000 psig. Proper selection of the processing scheme, operating temperature, pressure, and solvent rate, permits the process to be adjusted to selectively remove H_2S and CO_2 separately and to meet particular purified gas requirements.

Purification Limits

When treating a typical gas produced by coal or oil gasification, containing 1% H_2S and COS and 35% CO_2 (after shift), the process can yield a purified gas containing less than 0.1 ppm H_2S and COS and 1 ppm CO_2. Exact amounts removed depend upon the selection of the processing scheme and operating conditions. The process normally yields a concentrated H_2S and COS feed for a Claus plant and a CO_2 and N_2 stream that can be vented.

Utility Requirements[4]

Typical requirements, per MM scf of gas processed, when processing a feed gas containing 1% H_2S and COS and 5-6% CO_2 initially, and 36% CO_2 after shift, at 685 psig are given below. The purified gas contains less than 0.1 ppm H_2S and COS, and 0.1% CO_2

Steam, 70 psig, saturated, lb/MM scf	2,550
Cooling Water @ 75 °F, gal/MM scf	121,000
Electric Power (without recovery), kWh/MM scf	550
Solvent Loss, lb/MM scf	40
Waste Heat for Refrigeration MM Btu/MM scf	11
Stripping Gas (N_2), scf/MM scf	77,700

Environmental Considerations

The H_2S off-gas, which has high concentrations of H_2S and COS, will be processed in a sulfur recovery plant, such as a Claus unit. Under normal circumstances, the CO_2 and N_2 can be exhausted to the atmosphere. The CO_2 is 99.5% pure and may be used for urea synthesis. Solvent degradation is minimal, and waste liquid effluents are not produced.

Remarks

Rectisol is a well proven process for purifying gases from coal and oil gasification plants. Besides removing H_2S, COS, and CO_2, it also removes other unidentified compounds that are often encountered in coal conversion plants. It normally yields a H_2S-rich stream that can be readily processed in a Claus unit and a CO_2-N_2 stream that can be exhausted to the atmosphere. It is a physical absorption process, and the solution recirculation rate depends on the prevailing temperatures and pressures; the concentration of acid gases in the feed gas does not affect the circulation rate. The process operates at very low temperature levels, and gases are usually precooled prior to processing in the Rectisol unit.

References

1. "Gas Processing Handbook," Hydrocarbon Processing, April 1979, p. 118.
2. Hochgesand, G., "Rectisol and Purisol," Industrial and Engineering Chemistry, 62(7), July 1970, pp. 37-43.
3. Riesenfeld, F. C., and Kohl, A. L., "Gas Purification," 2nd Edition, Gulf Publishing Company, Houston, Texas, 1974.
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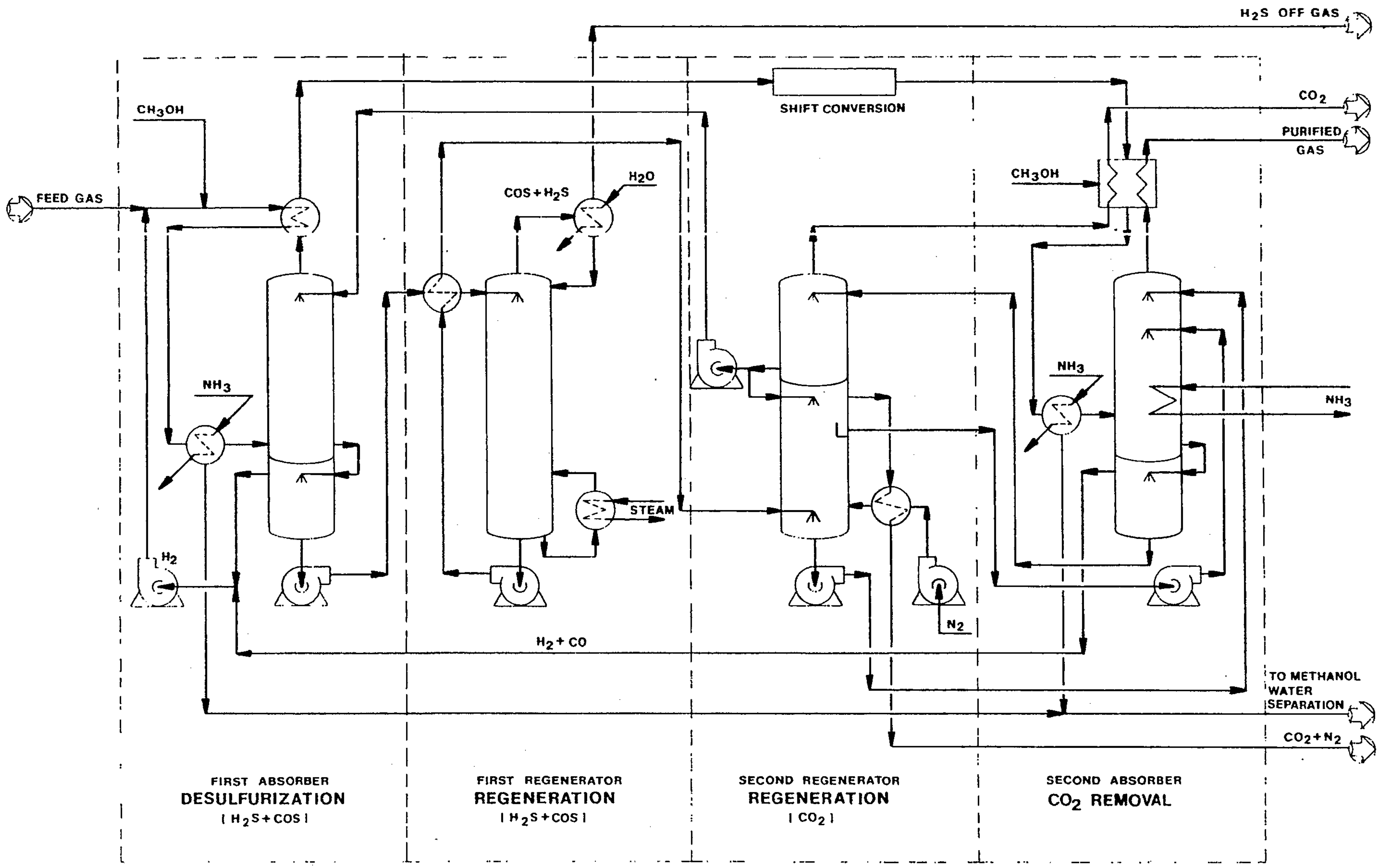

Figure 3A.17-1 Rectisol Process.

3A.18 SCOT

Licensor

Shell Development Company
One Shell Plaza
P.O. Box 2463
Houston, TX 77001

State of Development[1,2]

Like the Beavon process (Chapter 3A.5), the SCOT (Shell Claus off-gas treating) process is designed to handle the tail gases from a Claus plant. The two processes are similar initially in that they both use catalytic hydrogenation over a cobalt-molybdenum catalyst to convert sulfur compounds in the gas to H_2S. However, they differ in the final step; whereas the Beavon process uses a Stretford unit to convert the H_2S to sulfur, the SCOT process uses selective amine absorption (usually di-isopropanolamine) and recycles the stripped acid gases to the Claus plant.

The SCOT process was developed by the Royal Dutch Shell Laboratories in the Netherlands and was made available for use by industry in 1972. Licensing of the process in the United States is handled by Shell Development Company in Houston, Texas. The first two commercial units, built in 1973 in California at the refineries of Champlin Petroleum and Douglas Oil, were small skid-mounted installations. These units had Claus plant capacities of 15 and 9 long tpd of sulfur respectively. Many other SCOT units are now in use or are under construction, handling tail gases from Claus plants ranging in size from 4 to 2100 long tpd of sulfur.

As of April 1981, there were 53 committed projects in the U.S.A.: 27 in operation, and 26 others in various stages of design or construction. For the rest of the world there were 31 announced units: 21 in operation and 10 others in various stages of construction.

Process Description[1,2,3]

The SCOT process is shown schematically in Figure 3A.18-1. Claus tailgas is heated to about 570 °F in a heater or an in-line burner along with H_2 or a mixture of H_2 and CO. This reducing gas may be supplied either from an outside source or from substoichiometric combustion in the in-line burner. The combined gas stream is then passed into the top of a reactor containing a cobalt-molybdate on alumina catalyst. As the gases flow downward over the catalyst, the sulfur compounds, including SO_2, CS_2 and COS, are converted to H_2S. The gas then passes into a waste heat boiler, where it is cooled to about 330 °F by generating steam for use in plant operations. The gas is then cooled further to about 104 °F by countercurrent contact with water in either a trayed or packed column. During this step, excess water is condensed and removed from the process stream. Water from the quench column is typically sent to a sour water stripper.

Occasionally, additional pressure is needed to get the gas through the unit. In this case, a booster blower can be placed between the quench column and absorber. This blower may also be used effectively to circulate gas through the unit during start-up. The absorber column is used to preferentially extract H_2S from the gas stream. Relatively little CO_2 is co-absorbed with the H_2S. The absorbing material is generally a water solution of di-isopropanolamine (DIPA), although other alkanolamines may be used where large amounts of CO_2 are present. Countercurrent contact with amine solution over trays reduces the H_2S concentration in the gas from about 15,000 ppm to less than 200 ppm. Treated gas from the absorber is incinerated to assure that the H_2S is reduced to less than 10 ppmv by conversion to SO_2.

The rich amine solution, which leaves the bottom of the absorber, is heated by exchange with hot lean solution and then goes to a conventional solvent stripper, where it is stripped with steam generated in a steam-heated reboiler. The overhead is condensed to provide reflux, and the stripped acid gases from the top of the reflux drum are recycled back to the Claus plant feed.

Chemical Description[4]

SO_2 and elemental sulfur are first hydrogenated with the H_2-rich gas as follows:

$$SO_2 + 3H_2 \longrightarrow H_2S + 2H_2O$$
$$S_8 + 8H_2 \longrightarrow 8H_2S$$

When CO is present in the reducing gas stream, the following reactions may also occur

$$SO_2 + 3CO \longrightarrow COS + 2CO_2$$
$$S_8 + 8CO \longrightarrow 8COS$$
$$CO + H_2O \longleftrightarrow CO_2 + H_2$$
$$CO + H_2S \longleftrightarrow COS + H_2$$

COS and CS_2 are converted to H_2S as shown

$$COS + H_2O \longleftrightarrow CO_2 + H_2S$$
$$CS_2 + 2H_2O \longleftrightarrow CO_2 + 2H_2S$$

The H_2S and some of the CO_2 in the quench tower off-gas are absorbed by the amine (RNH_2) solution according to the following reactions:

$$RNH_2 + H_2S \longleftrightarrow RNH_3 \bullet HS$$
$$2RNH_2 + CO_2 + H_2O \longleftrightarrow (RNH_3)_2CO_3$$

When heat is applied in the stripper, the above reactions are reversed, freeing the acid gases.

Operability Limits[2]

The SCOT process is designed for about 5 psig pressure operation and low pressure drop so that it can be easily added to existing Claus plants. If pressure available is insufficient, a booster blower is often installed between the quench tower and the absorber. Amine absorption temperature is about 100 °F. The stripper normally operates at about 250 °F.

Purification Limits[1,2]

Claus plant tail-gases typically contain elemental sulfur, H_2S, COS, CS_2, SO_2, and CO_2. Inlet concentrations may be as much as 3% H_2S and 40% CO_2 or more. Purified gas exiting the absorber is typically reduced to 100-500 ppm of total sulfur as H_2S. About 10 to 20 % of the CO_2 is also absorbed.

Utility Requirements[1]

Typical utility requirements for a SCOT unit are shown below for a plant serving a [illegible]00 long tpd Claus plant

Steam @ 150 psig, lb/hr	6700
Cooling water (30 °F rise), gpm	960
Electric Power, kW	21
Fuel Gas, MM Btu/hr	2.2

Environmental Considerations

Acid gases exiting the SCOT stripper are recycled to the Claus plant feed. Purified tail gas from the absorber is incinerated before it is vented to the atmosphere. Sour condensate from the quench tower is stripped to remove dissolved H_2S and CO_2 before it is discharged.

Remarks

SCOT is a well proven process for Claus tail gas clean-up. It can also be used for purification of other industrial fuel gases. Acid gas from the SCOT stripper that is recycled to the Claus plant feed may tend to dilute the main Claus feed stream. However, the SCOT recycle is normally a small portion of the Claus feed, and the dilution is not significant. The process is flexible in that it can operate over a wide range of sulfur intake capacity.

References

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2. "The Scot Process," Brochure from Shell Development Co., 1980.
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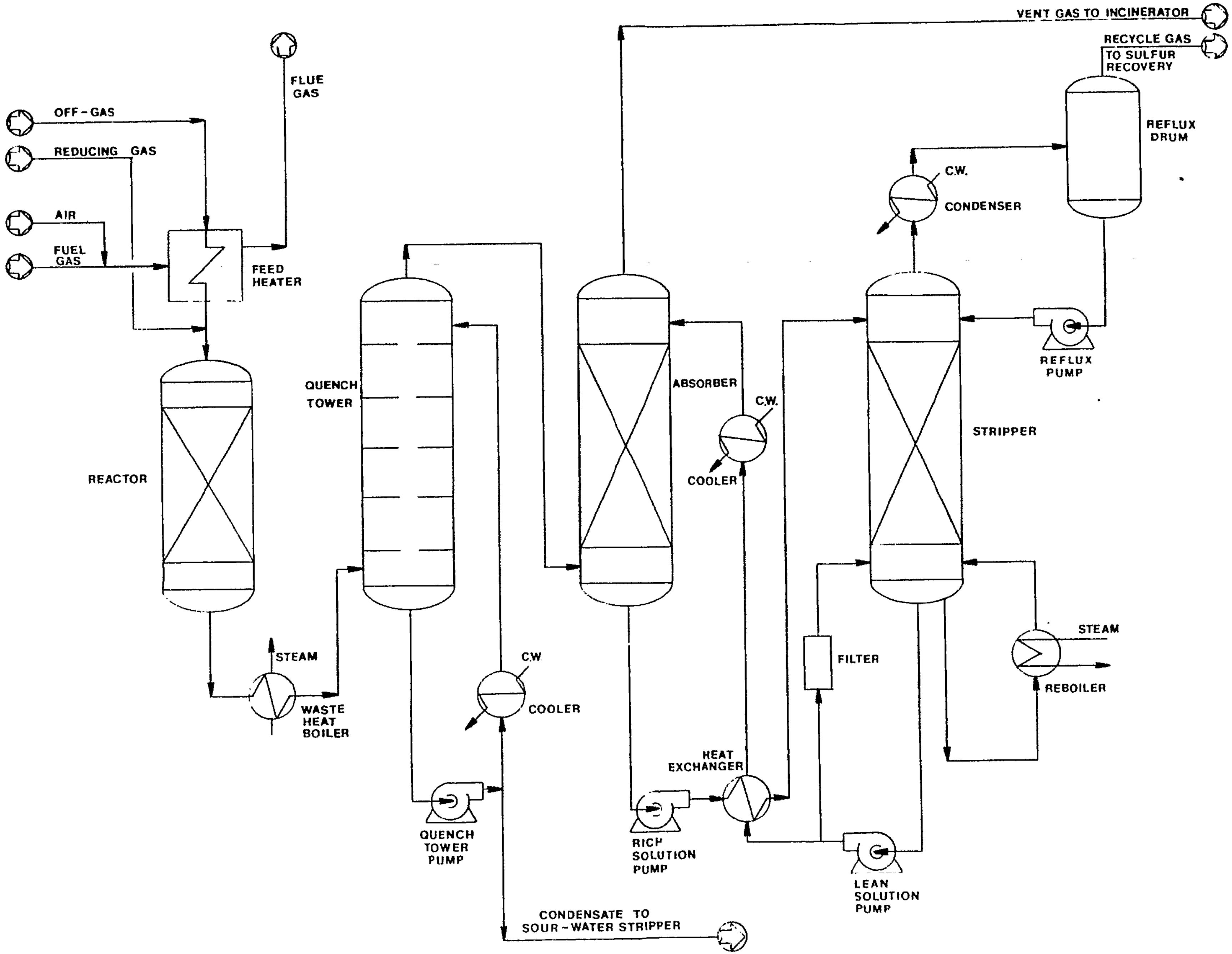

Figure 3A.18-1 Scot Process.

3A.19 SELEXOL SOLVENT

Licensor

Allied Chemical Corporation
Gas Purification Department
P.O. Box 1013R
Morristown, NJ 07960

State of Development

The Selexol Solvent process was developed by Allied Chemical Corporation in the early 1960s. The process uses Selexol Solvent (dimethyl ether of polyethylene glycol) to remove H_2S, CO_2, and other acidic and nonacidic components from industrial gases by physical absorption. Applications include sour natural gas; synthesis gas from the gasification of coal, oil, and light hydrocarbons; synthesis gases from steam reforming or partial oxidation; and refinery gases. The first commercial plant was put on stream in 1965 as part of an ammonia train at Allied's Omaha facility. Since then 22 other plants with capacities up to 275 MM scfd each have been put into operation or are under construction, processing a total of over 1240 MM scfd of sour feed gas. More than three Selexol units are in operation or in various stages of design in coal conversion applications.[1 pc]

Process Description[1 2]

In this process (Figure 3A.19-1), sour feed gas enters the bottom of the absorber, and both stripped and semistripped solvent are pumped to the top. The solvent absorbs the H_2S and some of the CO_2, COS, and mercaptans as it passes countercurrently to the gas. The purified gas exits at the absorber top.

Rich solvent exits the absorber bottom and may be passed through a power recovery turbine before flashing. Because the Selexol Solvent absorber is usually operated at a high pressure, flashing is often done in different stages to obtain different cuts of the dissolved gases. The number of stages selected depends upon the application.[3] For example, synthesis gas from a coal gasifier normally requires only one stage of flashing before stripping. If the feed gas contains light hydrocarbons, as many as three flashing stages may be used prior to stripping.

The high-pressure flash removes hydrocarbons and some CO_2. This flashed gas is compressed and recycled to the absorber with the feed gas to enhance the selectivity of the Selexol Solvent for sulfur compounds. In the lower-pressure flash tank, acid gases are desorbed merely by pressure reduction.

The bottom material from the low-pressure flash is fed to the stripper. In the stripper, the remaining acid gases are removed by stripping with steam or inert gas. Lean solvent is pumped from the stripper bottom to the absorber to continue the absorption process. The acid gases and stripping medium exiting the top of the stripper are sent to further processing.

Chemical Description

The Selexol Solvent process is a physical absorption process. The solvent has a high physical absorption capacity for sulfur-based compounds, including H_2S, COS, and mercaptans, as well as for CO_2. The solvent is not degraded by impurities in the feed gas; thus, no solvent reclaimer is required. In the stripper, the solvent is easily regenerated to less than 1 ppm H_2S by weight with steam or inert gas. This, combined with the low solvent vapor pressure, results in very low solvent losses.

Since the solvent also removes water from the feed gas, the process can meet pipeline dew point specifications simultaneously with acid gas removal.

Operability Limits[4]

The low heats of absorption involved in the process, together with Selexol Solvent's specific heat of 0.5, result in minimal external heating and cooling requirements. Many times, the temperature can be controlled by using only hydraulic and gas turbines and heat interchange. The absorber is normally operated between 500 and 1000 psig, since the higher pressure favors physical asborption. The pressures of the flash stages decrease in steps from the absorber pressure to the stripper pressure, which is about 0-5 psig. The distribution of the released acid gases depends upon the interchange flash pressure and the solvent loading. The absorber operating temperature range is 20-100 °F.

Purification Limits

Absorption of the impurities in the feed gas by Selexol Solvent is essentially proportional to their partial pressures. Feed conditions can therefore be varied over a wide range with the same equipment. The process can reduce the purified gas content to less than 1 ppm H_2S, 1 ppm COS, and 1 ppm mercaptan. The CO_2 can be retained or reduced to any required level. Selexol's different solvent loading (scf acid gas absorbed/gallon solvent) for H_2S and CO_2, combined with the optional use of recycle, allow the process to be adjusted to meet specific feed and purified gas requirements, including selective absorption of the sulfur compounds.

Utility Requirements

Typical utility requirements per MM scf when treating a gas containing about 1/2% H_2S and 35% CO_2 at 500 psig, which is reduced to less than 0.1 ppm H_2S and 11% CO_2 in the purified gas, are estimated to be

Steam, lb/MM scf	3,000
Cooling water, gal/MM scf	35,000
Electric Power, kWh/MM scf	900
Solvent Loss, lb/MM scf	0.5

In this example, the acid gas is removed after shift in two stages: the H_2S is removed first and then the CO_2.

Environmental Considerations

H_2S, COS, and other sulfur-based compounds in the acid gases exiting the low pressure flash require further processing in a sulfur recovery unit, such as a Claus. Stripping gas may or may not require treatment, depending on the application. The process does not produce waste effluents from chemical degradation of solvent.

Remarks

The process is highly selective to sulfur compounds and yields a high sulfur feed for the Claus plant. The solvent is physically and chemically stable, and plants can run on the same solvent without withdrawing any blowdown. Only mechanical losses have to be replaced. The dehydration obtained with the process can eliminate the necessity of a separate gas-dehydration facility, which is usually needed with aqueous-amine processes.

Since the process involves physical absorption, it is well suited for gases at high pressures with high acid gas concentrations. However, a gas at a low pressure and/or with a low concentration of acid gases may have to be treated in one of the other processes. Also, because the absorption is physical, hydrocarbons are absorbed in amounts proportional to their partial pressure, and extra handling of the Selexol Solvent is required to separate them.

References

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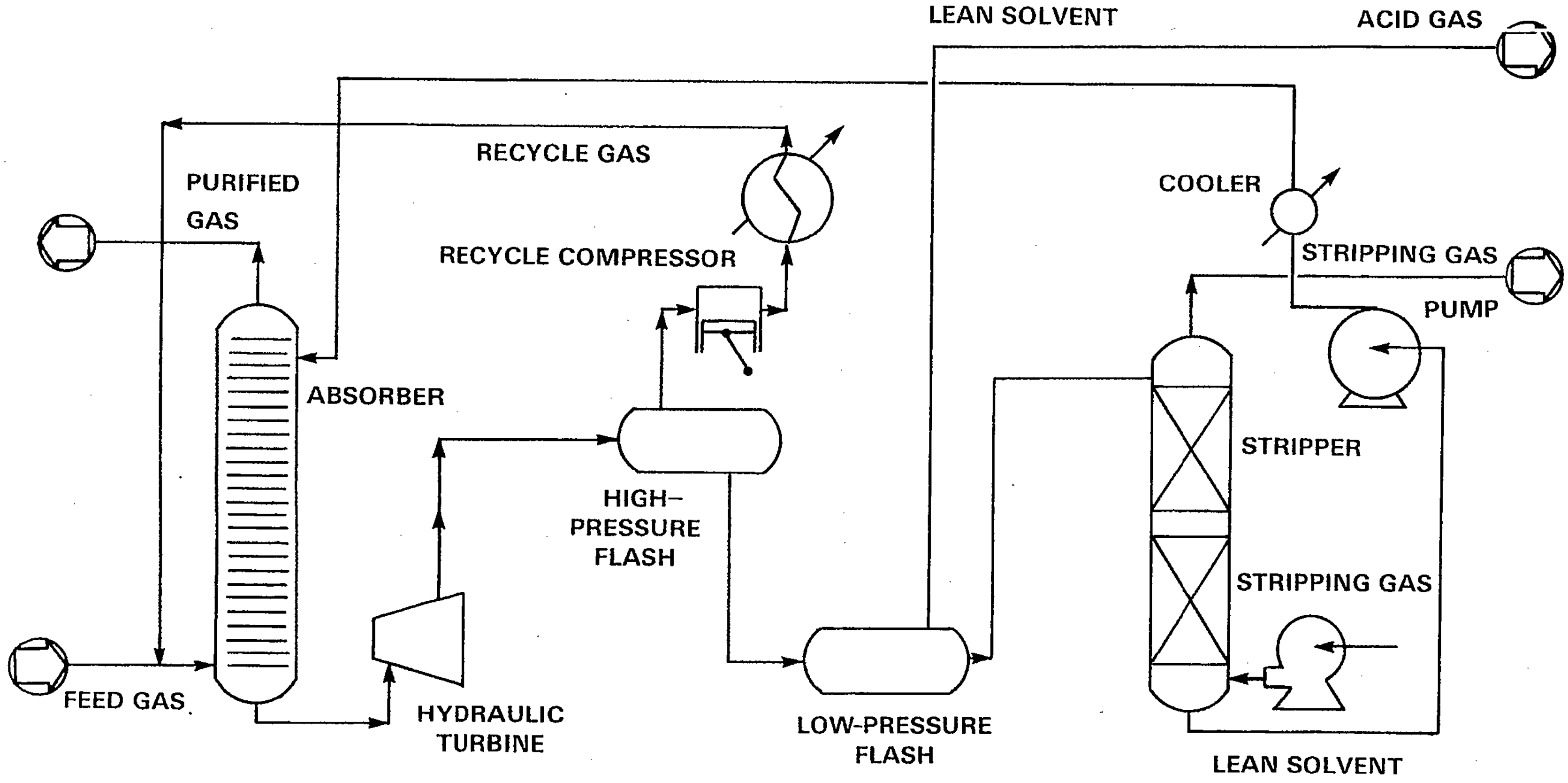

Figure 3A.19-1 Selexol Solvent Process

3A.20 SNPA-DEA

Licensor

Ralph M. Parsons Co.
100 W. Walnut Street
Pasadena, California 91124

State of Development

Many alkanolamine compounds are available as possible acid gas absorbents to remove carbon dioxide and hydrogen sulfide. Two processes using these compounds -the MEA and MDEA processes - have already been described in this handbook in Chapters 3A.14 and 3A.15. Another commonly used alkanolamine is Diethanolamine (DEA).

Aqueous solutions of DEA are being used for the treatment of refinery gases, which normally contain appreciable amounts of COS and CO_2 in addition to H_2S and CO_2. Aqueous solutions of DEA have also been used successfully for the treatment of natural gas by the Societe National des Petroles d' Aquitaine (SNPA). As a result of SNPA's experience, the SNPA-DEA process has been widely accepted for the treatment of high-pressure natural gases with high concentrations of acidic components, especially if COS and CS_2 are also present in appreciable amounts.[1] The SNPA-DEA process is currently used to remove acid gases from over 5 billion scfd of raw gas.

Process Description[2 3]

As shown in Fig. 3A.21-l, an SNPA-DEA unit is similar to any other conventional amine unit. In this process, sour raw gas enters the absorber, where it is scrubbed with a lean DEA solution in countercurrent flow. The H_2S and CO_2 are absorbed in the rich DEA solution drawn from the bottom of the absorber. Rich DEA solution then goes to a flash tank, where the dissolved hydrocarbons are released at a low pressure. The flash gas is further purified before using it as a fuel. The liquid stream from the flash tank is preheated by the exchange of heat with hot lean solution from the regenerator. In the regenerator, the acid gases are stripped from the DEA solution, then cooled and routed to a sulfur recovery plant. Condensate from cooling of acid gas stream is refluxed back to the regenerator. Heat input to the regenerator is from low-pressure steam used in the reboilers. Lean DEA from the regenerator is cooled by exchanging heat with DEA cold rich solution and then with a water cooler. The cold lean solution then is pumped to the top of the absorber to complete the closed loop absorption-regeneration cycle.

Chemical Description[1]

DEA is a secondary amine in which the alkane groups of the amine reduce the vapor pressure and increase the water solubility, while the amino group provides the necessary alkalinity in the water solutions to cause the absorption of acidic gases. Because of its low vapor pressure, DEA is suitable for low-pressure operation, and it is also less reactive with COS and CS_2 than are other amines.

The typical reversible absorption-regeneration reactions of acid gases with DEA (R_2NH) are expressed by:

$$R_2NH + H_2S \longleftrightarrow R_2NH_2 \bullet HS$$
$$R_2NH + CO_2 \longleftrightarrow R_2NH_3 \bullet HCO_3$$

At high partial pressure of acid gases, an aqueous solution containing 20% to 30% wt of DEA absorbs acid gases to near the stoichiometric molar ratio. Typical DEA systems operate at the ratio range of 1.0 to 1.3 moles of DEA per mole of acid gas.

Operability Limits[4]

Commercial DEA plants are presently in operation at pressure ranges from 600 to 1100 psig for raw gas streams containing 11% to 35% of acid gases, in which the ratio of H_2S/CO_2 varies from 34 to 0.65.

The heat of reaction of acid gases to DEA is lower than to MEA. Therefore, compared with MEA, acid gas stripping is easier in DEA regeneration, and less vigorous reboiling is required. The absorber and regenerator temperatures of a DEA unit are about the same as those of the MEA process.

Purification Limits

The DEA process can reduce acid gas concentrations to less than 3 ppm H_2S and 500 ppm CO_2 in the natural gas. The presence of COS and CS_2 will not deteriorate the solution. The decomposition products during the absorption and regeneration are easily removed by filtration through activated carbon. Purified gas can meet pipeline gas specification by proper selection of process parameters.

Utility Requirements

The utility requirements of the DEA process are not available.

Environmental Considerations

The DEA process is normally designed for a non-selective chemical absorption process. The acid gases stream requires use of a sulfur recovery system. The solvent blowdown stream consists primarily of traces of solvent degradation products and other components scrubbed from the feed gas. Disposition of this stream will be determined by the nature of the impurities present and the nature of treatment required.

Remarks

DEA is a widely used alkanolamine process. The process is preferred for removing high sulfur content acid gas from high-pressure sour gas streams, especially for sour gas containing COS and CS_2.

DEA may also effectively remove traces of COS, CS_2, and other organic sulfur besides H_2S and CO_2. The solution is mildly corrosive. The chemical losses are minimized by proper design of the acid gas removal system.

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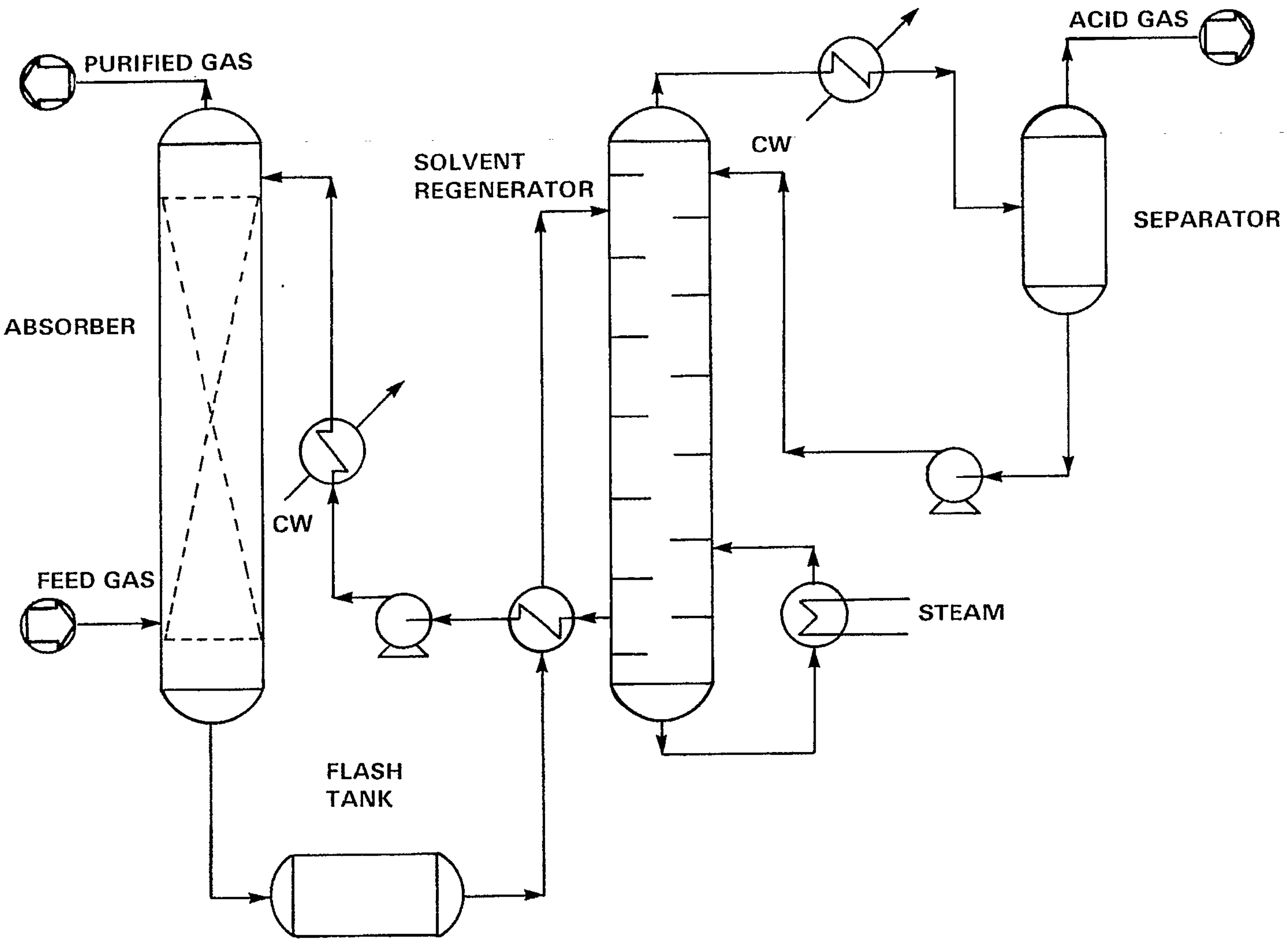

Figure 3A.20-1 SNPA-DEA Process.

3A.21 STRETFORD

Licensors

Various engineering and construction firms license the basic Stretford Process. Each firm incorporates refinements it has developed. These refinements are aimed primarily at reducing the amounts of waste streams and reagent usage. Holmes-Stretford process, a modification of the basic process, is licensed by Peabody Process Systems of 835 Hope Street, Stamford, CT 06907.

State of Development

The Stretford process was originally developed by the North Western Gas Board of the British Gas Corporation. The process removes H_2S from gas streams by chemical absorption. A number of improvements and refinements have been made in the basic Stretford process by various firms and have been applied to commercial gas purification operations. Over 50 plants are currently in operation worldwide, purifying refinery gas, producer gas, coal gas, synthesis gas, coke oven gas, and geothermal steam incondensibles. Plant capacity ranges from 0.1 to 200 MM scfd of feed gas with sulfur removal rates from 0.5 to 90 long tpd. Peabody has built 17 units that desulfurize coal-derived gases.[1]

Many of the Stretford process plants currently in operation are either low pressure or near atmospheric. Higher-pressure installations (up to 300 psig) are in operation for natural gas sweetening and for sulfur recovery from fixed bed high-pressure gasifiers.

An important problem connected with the Stretford process is the treatment and disposal of effluent streams containing sodium thiocyanate (from HCN in the feed gas), sodium thiosulfate, and sodium sulfate. A number of schemes to handle the effluent streams have been successfully demonstrated in pilot plant and semi-commercial operations. One of these schemes is reductive incineration. In this scheme, waste products are treated and recycled, and it is reported that no waste products requiring disposal are produced.

Process Description[2]

The purpose of the Stretford process is to remove H_2S from gas streams and recover the sulfur in elemental form. Theoretically, if H_2S were the only acid gas present and no side reactions occurred, the Stretford process could operate without producing any waste chemical streams requiring disposal or special treatment. However, gas streams from coal processing generally contain some HCN and small amounts of other sulfur compounds. Some of these compounds and HCN react in an irreversible manner with the Stretford chemicals.

There are two variations of the Stretford process that differ in the way HCN is removed. In the first variation, the HCN is removed from the gas in a separate column before the removal of the H_2S. In the second variation, the H_2S and HCN are removed in the same absorber. The first variation is higher in capital cost but lower in operating cost, especially with respect to chemical usage. The processing scheme selected for a given application depends primarily on the concentration of HCN in the gas. When this concentration is high (e.g., coke oven gas) a separate HCN-removal step is justifiable. In coal gasification, the concentration of HCN is too small to justify a separate HCN-removal step.

Figure 3A.20-1 is a simplified schematic flow diagram of a typical Stretford plant in which H_2S and HCN are removed in the same absorber and the wastes are treated by reductive incineration.

The feed gas to be cleaned enters the bottom of the absorber, and regenerated alkaline Stretford solution is pumped to the top. The solution absorbs the H_2S, HCN, and SO_2 from the gas as it passes countercurrently. The CO_2, however, is only partially absorbed. Upon absorption, the H_2S is oxidized to elemental sulfur by the vanadic salt in the solution, while the salt, in turn, is reduced to the vanadous form. The purified gas exits at the absorber top.

The reduced liquor from the absorber flows to the primary and secondary oxidizers, where the vanadium is restored to its vanadic form by a redox mechanism using as catalyst anthraquinone-disulfonic acid (ADA). In these oxidizers, air is blown through a liquor to reoxidize the ADA and separate the sulfur by froth flotation.

The sulfur froth flows to the sulfur slurry tank by gravity. The liquor, which is the regenerated Stretford solution, together with any makeup solution required, is pumped to an interchanger, where (in summer) it is cooled before entering the absorber to continue the absorption reaction.

Sulfur from the slurry tank is pumped to a centrifuge (or filter). Cake from the centrifuge is discharged to a reslurry tank, where it is reslurried with process water or recycle liquor from the sulfur separator. The reslurry operation serves to reduce the Stretford reagent loss and results in a purer sulfur product. Filtrate from the centrifuge is pumped back to the pumping tank.

Sulfur slurry from the reslurry tank is pumped to a sulfur heater, where the sulfur is melted. The slurry then enters a sulfur separator, where the molten sulfur and recycle liquor are decanted. The molten sulfur (99.5% purity) is continuously withdrawn to storage. Part of the separated hot liquor is recycled to the reslurry tank; the remainder flows to the effluent storage tank.

Sodium thiocyanate, sodium thiosulfate, and sodium sulfate are produced during the absorption and regeneration reactions. These undesirable salts could build up to unacceptable levels in the Stretford solution; therefore, it is necessary to remove a proportion of the solution as effluent. Because the effluent contains vanadium salts together with the salts mentioned above, it must be treated prior to discharge. There are several ways to treat this effluent, and a number of proprietary schemes have been developed. Reductive incineration, one of these, is shown in Figure 3A.20-1.

In the reductive incineration method, effluent pumped from the storage tank is burned with deficient air and a feed gas (usually a small stream taken from the main feed to the Stretford plant). This incineration produces a gas (containing CO, CO_2, N_2, H_2S) that is recycled to the absorber feed gas inlet, and regenerated salts that are returned to the solution in the absorber base. It is reported that this process results in no effluent discharge because all of the products from this step can be recycled.

Such a reductive incineration scheme is required especially when treating high-HCN-content gas, such as coke oven gas, which contains over 1000 ppm of HCN. For gases with a low HCN content, the scheme may not be necessary. In coal conversion plants the blow-down can be used for coal ash quenching or it may be partially evaporated and added to the coal feed.

Chemical Description[3]

A typical Stretford solution consists of an aqueous solution of the following chemicals

ADA (anthraquinone-disulfonic acid)
Vanadium (as sodium metavanadate)
Sodium carbonate

With time, presence of sodium thiosulfate (and thiocyanate) and sulfate will be significant. Part of the sodium carbonate becomes bicarbonate.

H₂S Removal

H_2S is dissolved and ionized as HS^- by sodium carbonate in the circulating liquor and is then oxidized to free elemental sulfur by the reduction of vanadium from the pentavalent state to its quadrivalent state. The reduced vanadium is subsequently oxidized by a redox mechanism with ADA, which itself is reoxidized by oxygen in the air to complete the cycle. The following overall chemical reactions take place:

$$2H_2S + 2Na_2CO_3 \longrightarrow 2NaHS + 2NaHCO_3$$
$$2NaHS + 4NaVO_3 + H_2O \longrightarrow Na_2V_4O_9 + 4NaOH + 2S$$
$$Na_2V_4O_9 + 2NaOH + H_2O + 2ADA \longrightarrow 4NaVO_3 + \underset{\text{(reduced)}}{2ADA}$$
$$2NaHCO_3 + 2NaOH \longrightarrow 2Na_2CO_3 + 2H_2O$$
$$2ADA\text{(reduced)} + O_2 \longrightarrow 2ADA + 2H_2O$$
$$2H_2S + O_2 \longrightarrow 2H_2O + 2S$$

HCN Removal

The chemical reagents used in the Stretford process react irreversibly with HCN to produce sodium thiocyanate (NaCNS), which accumulates in the recirculating solution and must be removed as a waste effluent. Therefore, in some Stretford process applications, the HCN in the feed gas stream is removed separately before the gas stream enters the H_2S absorber. This is accomplished by reacting HCN with sodium polysulfide ($Na_2S_{(n+1)}$) solution in a separate absorber. The required sodium polysulfide is formed in a separate polysulfide generator. Polysulfide formation, HCN removal, and polysulfide regeneration take place according to the following reactions:

$$Na_2CO_3 + H_2S \longrightarrow Na_2S + CO_2 + H_2O$$
$$Na_2S + nS \longrightarrow Na_2S_{(n+1)}\text{(formation)}$$
$$HCN + Na_2S_{(n+1)} + Na_2CO_3 \longrightarrow NaCNS + NaHCO_3 + Na_2S_n$$
$$Na_2S_n + S \longrightarrow Na_2S_{(n+1)}\text{ (regeneration)}$$

With either separate or simultaneous removal of the HCN and H_2S, a small effluent slip stream must be taken to prevent NaCNS build up. However, if the HCN is treated separately there will be a smaller loss of the more valuable Stretford solution.

Thiosulfate and Sulfate Formation

The H_2S in the Stretford solution reacts in part with O_2 in the oxidizers to form $Na_2S_2O_3$ as follows:

$$2H_2S + 3/2\ O_2 + Na_2CO_3 \longrightarrow Na_2S_2O_3 + CO_2 + 2H_2O$$

If SO_2 is present in the feed gas, it reacts with the solution to form Na_2SO_3 as follows:

$$SO_2 + Na_2CO_3 \longleftrightarrow Na_2SO_3 + CO_2$$

The $Na_2S_2O_3$ and Na_2SO_3 accumulate in the recirculating solution and must be removed in the bleed stream.

Operability Limits

Operating pressures of Stretford plants vary from near atmospheric to 100 psig in the absorber. The solution oxidizer and sulfur recovery systems operate at atmospheric pressure. Feed gas temperatures are in the range of 80 to 120 °F.

Inlet H_2S concentrations as low as 300 ppm and as high as 95% can be processed. The process can tolerate CO_2 in any amount, and HCN concentrations as high as 2000 ppm can be handled.

Purification Limits

In the Stretford process, H_2S concentrations in the purified gas can be reduced to less than 1 ppm. Virtually complete removal of HCN is obtained. The Stretford process does not significantly remove CO_2 from the feed gas. A large proportion of methyl mercaptan is removed by the process, but COS and CS_2 are not reduced to a significant degree.

Utility Requirements

The utility requirements for the Holmes-Stretford unit using the reductive incineration on the basis of 1 long tpd of sulfur recovered are[2]

Steam, lb/day	1613
Process water gal/day	9770
Electric Power, kWh/day	1670
Fuel Gas, MM Btu/day	3.96

Typical chemical requirements without separate HCN removal but with reductive incineration are estimated as follows (basis: 1 long tpd of sulfur recovered)

ADA, lb/day	2.5

Environmental Considerations

An effluent stream of Stretford solution is required to prevent excess build up of cyanates and thiosalts. This stream contains vanadium salts, sodium thiocyanate, sodium thiosulfate, and sulfate, and therefore it must be treated prior to discharge. Four proprietary alternative methods have been developed and piloted:

1. Evaporative or spray drying
2. Biological degradation
3. Oxidative combustion
4. Reductive incineration

It is reported that reductive incineration will result in essentially zero effluent discharge because all the products are recycled. Small amounts of ADA are decomposed to H_2O and CO_2 in the reductive incineration and must be replaced. All the vanadium is recovered and all the sodium salts are converted to sodium carbonate.

Remarks

The Stretford process selectively removes H_2S from feed gas and yields elemental sulfur as a product in one integrated step. The sulfur level in the purified gas can be as low as 1 ppm. The process is capable of high turndown ratios.

The vanadium and other salts produced as waste must be properly treated. Several available methods of treatment should be evaluated for each particular installation before final selection. If a significant level of HCN is present in the feed gas, either a separate column is required for its removal or heavy consumption of soda ash is incurred.

Among the process limitations are that it does not remove organic sulfur compounds, except for minor quantities of methyl mercaptans; high CO_2 partial pressure in the feed gas causes the system to operate at lower pH's, reducing the efficiency of the process; and if the system becomes overloaded, i.e., H_2S concentration in the feed gas removal rate is greater than the design rate, an undesirable side reaction forming nonregenerable thiosulfate can become significant, requiring excessive scrubbing liquor blowdown rates.

References

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2. Vasan, S., "Holmes-Stretford Process," presented at The Canadian Natural Gas Processing Association, Edmonton, Canada, June 9, 1977.
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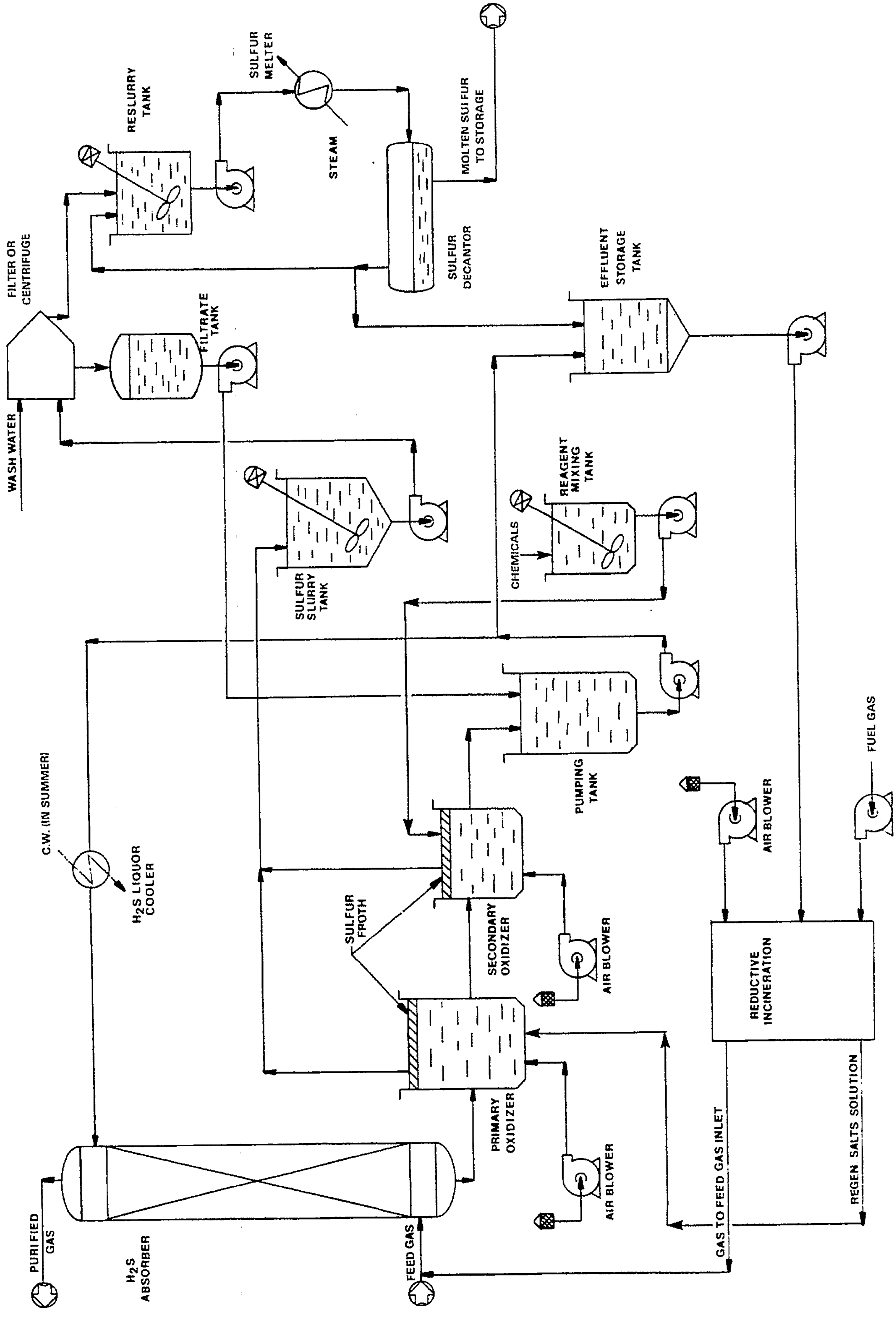

Figure 3A.21-1 Single Column Stretford Process.

3A.22 SULFIBAN

Licensor

Black, Sivalls, and Bryson, Inc.
B.S.& B. Process Systems Division
8303 S.W. Freeway
Houston, TX 77074

State of Development

The Sulfiban process was developed by Black, Sivalls, and Bryson, Inc. (B.S.& B.) in the early 1950s. The process uses an aqueous solution of monoethanolamine (MEA) to remove H_2S from industrial gases. Other acidic components can also be removed if the proper operating conditions are selected. Proprietary inhibitors are added to the solution to minimize MEA degradation and corrosion of process equipment. This basic MEA system is a standard of the gas purification industry. It is efficient in the removal of organic sulfides and has been used to desulfurize refinery gas, coke oven gas, synthesis gas, natural gas, and hydrogen in several hundred plants worldwide. More than 100 of these have been constructed by B.S.& B. since 1954 with individual capacities ranging from 0.2 to 200 MM scfd and totaling over 1.75 billion scfd.[pc]

Process Description[1]

The Sulfiban process is shown schematically in Figure 3A.22-1. The feed gas to be cleaned enters the bottom of the absorber, and an aqueous solution of MEA (12-20 wt%) is pumped to the top. This lean solution absorbs most of the H_2S, COS, CS_2, and HCN and some of the CO_2 as it passes countercurrent to the gas. The purified gas exits at the absorber top.

Rich solution containing absorbed acid gases is pumped from the absorber bottom and heated to 180-200 °F by interchange with the hot lean solution. It then flows to a stripper, where the absorption reactions are reversed by heat supplied by stripping steam generated in the reboiler. As the steam passes countercurrently to the rich solution, regenerated acid gases are driven overhead. Steam is then condensed, separated from the acid gases, and refluxed to the stripper, while the acid gases go to sulfur recovery as sulfur or sulfuric acid.

A portion of hot lean solution is withdrawn from the stripper bottom and fed to a redistillation unit. Here the spent amines, degraded by reactions with HCN and O_2 and/or organic sulfides, are recovered by distillation at higher temperatures. Unrecovered amines form a sludge, which is pumped to a settling tank and sent to disposal. Recovered amines pass overhead from the redistillation unit and return to the stripper.

The hot lean solution is pumped from the stripper bottom and cooled by interchange with the cool rich solution. It is then further cooled in a water-cooled exchanger and returned to the absorber.

Chemical Description[1] [2]

The H_2S, HCN, organic sulfides and a portion of the CO_2 are chemically absorbed from the gas in a 12-20% by weight aqueous solution of mono-ethanolamine ($HOCH_2CH_2NH_2$). Representing MEA as RNH_2, normal absorption reactions proceed as follows:

$$RNH_2 + H_2S \longleftrightarrow RNH_3 \bullet HS \text{ (in solution)}$$
$$RNH_2 + HCN \longleftrightarrow RNH_3 \bullet CN \text{ (in solution)}$$
$$2RNH_2 + CO_2 + H_2O \longleftrightarrow (RNH_3)_2 \bullet CO_3 \text{ (in solution)}$$

When heat is applied in the stripper, the above reactions are reversed, freeing the acid gas. However, reactions between MEA and organic sulfides such as CS_2 and COS are not reversible. Also, if any O_2 is present in the system, an irreversible side reaction between the MEA, HCN, and O_2 will take place, producing amine thiocyanates ($RNH_3 \bullet CNS$) or thiosulfates ($(RNH_3)_2S_2O_3$). The extent of these irreversible reactions can be minimized by maintaining the proper concentration of additives in the recirculating liquor.

Not all of the MEA is recovered in the stripper. Normally, a side stream is diverted to the reclaim reboiler, where the degraded amine and metal contaminants such as sodium, calcium, and iron are periodically discarded. For plants using a 15 to 20% solution of MEA and treating average sour gases, MEA consumption will vary from approximately 0.6 to 1.6 pounds per MM scf of sour gas as the operating pressure varies from 200 to 40 psig.[pc]

Since the process is based on chemical rather than physical equilibrium, the total loading of the rich solution should never exceed the reacting value of the amines for H_2S and CO_2 shown by the equations above. Using the reacting values with an allowance for acid gas left in solution after regeneration, the allowable pickup of acid gases by the MEA in commercial units is approximately 1.75 scf for every 10 wt% amine in solution. This relation is based on keeping the H_2S content of the treated gas below the maximum permissible and appears to hold over a wide range of pressures and acid gas contents.

Operability Limits

The heats of reaction and possible degradation of MEA at higher temperatures limit the operating temperatures. The temperature in the absorber is usually 100 °F, in the stripper, 200-250 °F, and in the redistillation unit, 250-300 °F. The feed gas should be at 60-100 °F to maintain the reactions and operating temperature limits. The absorber will operate over a wide feed gas pressure range - 0-1000 psig. The stripper and redistillation unit usually operate at 7-10 psig pressure. The process can be adapted for the treatment of various feed gas contents and rates and outlet gas concentrations by selecting proper operating conditions.

Purification Limits

The process can reduce H_2S content to about 1 ppm. Typically, the H_2S and HCN concentrations are reduced by greater than 98%. Other acid gases are removed to a lesser extent. The exact amounts of H_2S, CO_2, COS, HCN, or CS_2 removed depend upon the actual operating conditions.

Utility Requirements

Typical utility requirements per MM scf of feed gas at 40 psig, containing about 1.7% H_2S, 9.7% CO_2, 20 ppm HCN, and 300 ppm COS, are estimated to be as follows (the purified gas contains 2 ppm H_2S, a negligible amount of HCN, and CO_2 and COS at ppm levels)

Steam, lb/MM scf	8,200
Cooling Water, gal/MM scf	90,000
Electric Power, kWh/MM scf	50
Solvent (MEA) Loss, lb/MM scf	1.6

The above feed and purified gas concentrations are for a typical coal gasification application. In the case of a coke oven gas application, the H_2S and CO_2 concentrations are lower, the purified gas requirements are less stringent, and therefore the utility requirements are lower. The Sulfiban process can be used for either application but requires specific design modifications for each application.

Environmental Considerations

The acid gases exiting the stripper require further processing in a sulfur recovery unit, such as a Claus. Final disposition of amine sludges generated in the process must be determined for each installation. In coal conversion plants, they are generally mixed with waste ash. The amine sludge is not classified as a hazardous waste.

Remarks

The Sulfiban process can handle gases at low pressures, since the absorption is chemical rather than physical. At this low pressure, it can reduce H_2S concentration to about 15 ppm. The process does not remove hydrocarbons present in the feed gas.

The temperature of the feed gas should must be below 100°F. Solvent degradation occurs if COS and HCN are present in the feed gas. Even if only H_2S and CO_2 are present in the feed gas, some COS is formed from their interaction, and some solvent loss occurs.

References

1. Riesenfeld, F. C., and A. L. Kohl, "Gas Purification," 2nd Edition, Gulf Publishing Company, Houston, Texas, 1974.

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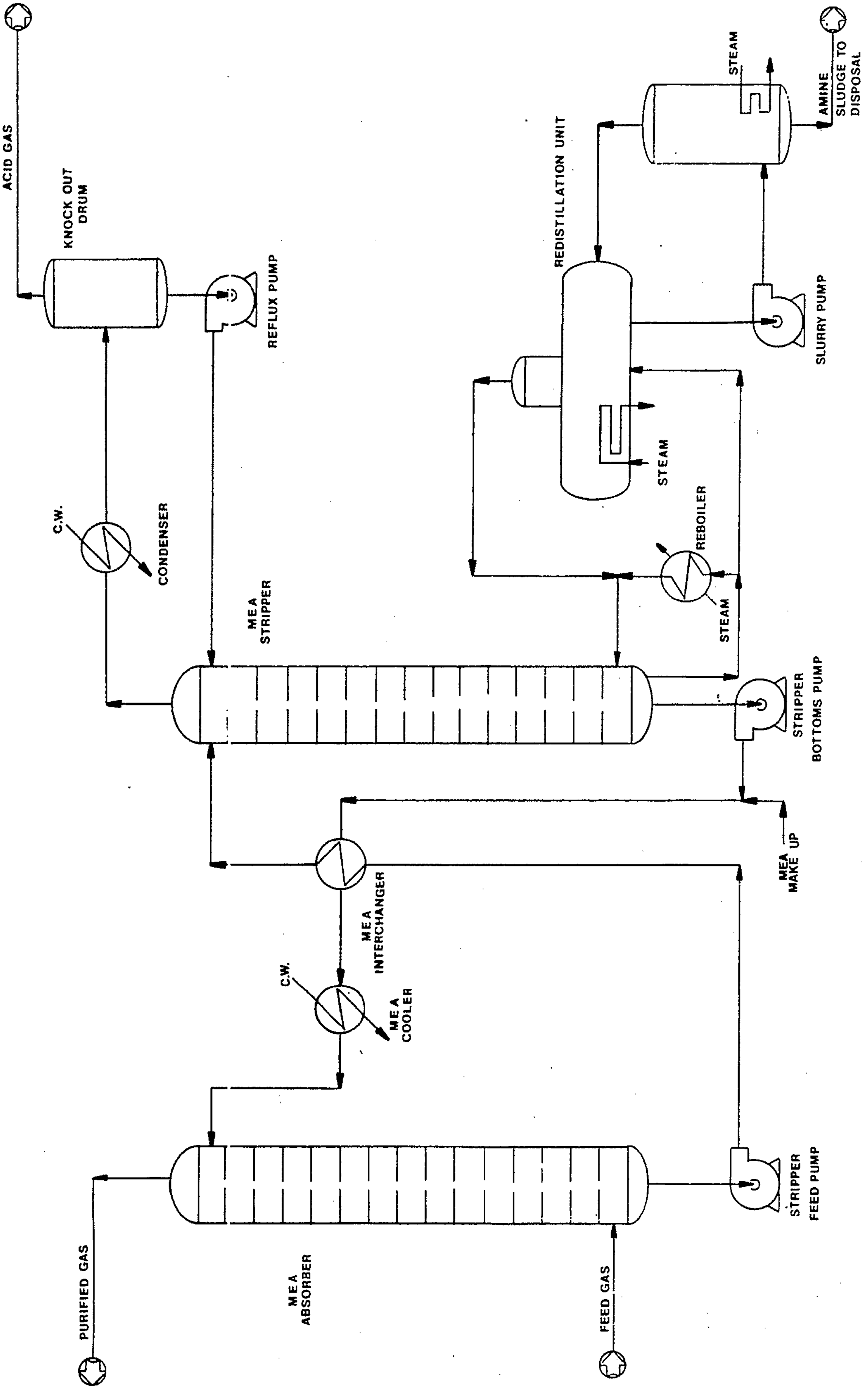

Figure 3A.22-1 Sulfiban Process.

3A.23 SULFINOL

Licensor

Shell Development Company
One Shell Plaza
P.O. Box 2463
Houston, TX 77001

State of Development[1]

The Sulfinol process was originally developed for treating gases very rich in H_2S. It uses a mixture of an organic physical solvent called Sulfolane (tetrahydrothiophene dioxide) mixed with an alkanolamine (di-isopropanolamine : DIPA), which is a chemical absorbent, and water. The first commercial application of the process was started in 1964 at the Person gas plant in Texas. Sulfinol process can effectively remove H_2S, CO_2, COS, CS_2, mercaptans and organic sulfides and disulfides from feed gas streams.

More than 100 units are in operation or under construction in U.S. and Canada (December 1980). Single location capacities vary from 15 to 500 MM scfd. The process is used for natural gas sweetening and for treating refinery gases, synthesis gases, LNG feedstocks, hydrogen, and ammonia plant reformer gas. Plants are in operation that remove H_2S and COS from partial oxidation gas in hydrogen generating plants and remove CO_2 from crude hydrogen for ammonia synthesis or for use in a hydrofining process.[1] pc

Process Description[2] [3] [4]

A typical flow diagram for the Sulfinol process is shown in Figure 3A.23-1. The feed gas to be cleaned enters the bottom of the absorber, and the solvent is pumped to the top. The solvent absorbs H_2S, CO_2, COS, and mercaptans both physically and chemically as it passes countercurrently to the gas. The purified gas exits at the absorber top.

At high pressure, appreciable amounts of other gas components (in addition to the acid gases) will be physically dissolved in the Sulfinol solution. The heavier hydrocarbons are absorbed in significant amounts, and even light hydrocarbons such as methane and ethane are absorbed to some degree. The rich Sulfinol solution can be sent to a flash tank after recovery of energy by pressure letdown through a power turbine. At the lower pressures encountered in the flash tank, most of the dissolved fuel-gas components are released. If the sulfur content of the flash gas exceeds allowable limits, a smaller scrubber can be incorporated into the process, treating the flash gas to the desired purity with a side stream of lean Sulfinol solution.

The rich solution leaving the flash tank is preheated (before entering the top of the regenerator) by heat exchange with lean solution from the bottom of the regenerator. The regenerator operates at near atmospheric pressure (typically 5 to 10 psig), and the absorber gases are stripped off by steam generated in a reboiler. Most of the water vapor in the regenerator overhead stream is condensed to provide reflux. The acid gases leave the top of the reflux drum. They may be sent to sulfur recovery is H_2S is present. Lean Sulfinol solution from the bottom of the regenerator is cooled by countercurrent heat exchange with the rich solution and, after cooling, is pumped to the top of the absorber. Degradation of the solvent is handled by sending a small stream to a steamheated reclaimer, from which the degradation products are rejected.

The lean solution cooler and reflux condenser are both shown in Figure 3A.23-1 to be water cooled. Air cooling can be substituted when minimization of cooling water usage is desired. Solution must be added to compensate for mechanical and vapor losses and for minor unreclaimable degradation losses of the amine constitutent of the Sulfinol solution.

When the Sulfinol process is used to treat gases at lower pressure and/or low hydrocarbon content, the intermediate flash step can be avoided. Here, the concern may not be so much the loss of valuable fuel components as the loss of hydrocarbon content of the regenerated acid gas.

Sulfinol solution is not degraded to any appreciable extent by COS or H_2S. However, CO_2 does react with DIPA to produce DIPA-Oxazolidone. The degradation product can be permitted to accumulate up to 10 wt% of the total DIPA in the Sulfinol solution without affecting plant operation. Regeneration of the degradation products may be accomplished in the solvent reclaimer, where feed rates are estimated at 0.1 to 0.5 gpm per 1000 gpm of solvent circulation.[4]

Chemical Description[4]

The Sulfinol solution contains a physical absorbent (Sulfolane) and a chemical absorbent (DIPA). The absorption/regeneration reactions of H_2S and CO_2 and DIPA can be expressed as:

$$R_2NH + H_2S \longleftrightarrow R_2NH_2 \bullet HS$$
$$R_2NH + CO_2 + H_2O \longleftrightarrow R_2NH_2 \bullet HCO_3$$

Because of the physical nature of Sulfolane, permissible solvent loading (i.e. mole acid gas/mole solvent) depends on the H_2S and CO_2 concentrations in the feed gas and on the operating pressure.

DIPA, like other alkanolamines, is subject to some chemical degradation by certain impurities (such as O_2 and HCN) that are present in some feeds. Carbon dioxide also degrades the DIPA to a small extent, depending upon CO_2 concentration, residence time, and temperature. No degradation of the Sulfolane has been detected nor, because of its recognized high stability, is any expected.

Operability Limits[3]

The pressure in the absorber may vary from slightly above atmospheric to 1400 psig. Higher-pressure operation favors physical absorption. The lean solvent temperature varies depending on the application and cooling available but is typically in the range 100-125 °F. The rich solvent temperature is higher because of heat of absorption. The process can be adapted for treatment of various feed gas contents, feed gas rates, and outlet gas concentrations by selecting proper solvent concentrations and other operating conditions.

Purification Limits[3]

The process has been used for natural gas applications in which the feed gas H_2S content varied from 0 to 53 mole% and CO_2 content from 1.[illegible] to 46 mole%. In the purified gas, H_2S can be reduced to less than 1 ppmv, CO_2 to less than 50 ppmv, and H_2S + COS to less than 3 to 5 ppmv by appropriate design.

Utility Requirements[4]

Typical requirements for a plant treating 13 MM scfd of feed gas containing 0.36 vol% H_2S, 5.2 vol% CO_2 and 125 ppm COS are given below. The treated gas contains 0.5 ppm H_2S, 25 ppm CO_2 and 0.3 ppm COS. The operating conditions are 573 psig, 104 °F absorber temperature, and 30 trays in the column.

Steam (@ 50 psi), lb/lb acid gas removed	1.9
Cooling Water, gal/MM scf feed	Not Available
Electric Power, kWh/ton acid gas removed	30

Environmental Considerations

The acid gases require further processing in a sulfur recovery unit, such as a Claus or Stretford. There is little degradation of organic sulfur compounds. Final disposition of the amine sludges generated in the process must be determined for each installation. In coal conversion plants, they are generally mixed with waste ash.

Remarks

The Sulfinol process combines physical absorption in Sulfolane and chemical absorption in DIPA. Thus, the solvent permits high acid gas loading at high pressure. Also, because of the chemical absorbent, the process can be used at low pressures. The corrosion and foaming problems are low and the solvent heat capacity is low.

Because a part of the solvent provides physical absorption, hydrocarbons in the feed gas are absorbed in the solution. Because a part of the solvent is chemical absorbent, utilities are higher than those required with solely physical solvents but lower than those required with aqueous amines.

References

1. "Sulfinol Process," brochure from Shell Development Co.
2. "Gas Processing Handbook," Hydrocarbon Processing, April 1979, p. 121.
3. Edwards, M.S., "H_2S Removal Processes for Low Btu Coal Gas," ORNL/TM-6077, Oak Ridge National Laboratory, 1979.
4. Singh, S. P. N., et al., "Costs and Technical Characteristics of Environmental Control Processes for Low-Btu Coal Gasification Processes," Oak Ridge National Laboratory, ORNL-5425, June 1980.

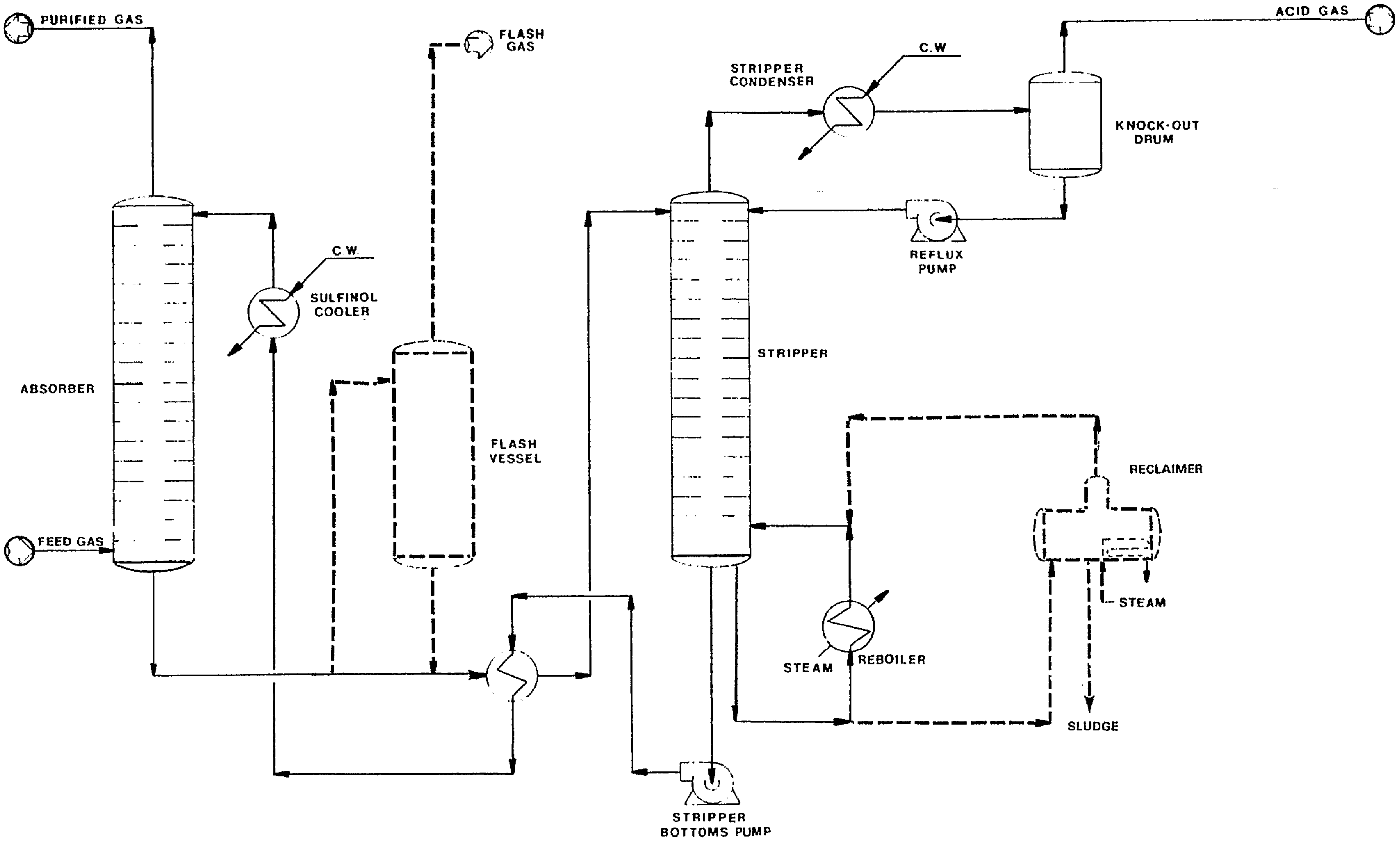

Figure 3A.23-1 Sulfinol Process.

3A.24 ZINC OXIDE ADSORPTION

Suppliers

1. United Catalysts, Inc.
   P.O. Box 32370
   Louisville, KY 40232

2. Katalco
   2901 Butterfield Rd.
   Oakbrook, Ill. 60521

3. The New Jersey Zinc Company
   65 East Elizabeth Avenue
   Bethlehem, PA 18018

State of Development

Zinc oxide adsorption is used in more than 100 commercial plants around the world in various types of natural gas and petrochemical operations.

Process Description[1]

This gas purification process consists simply of passing a gas through a bed of high surface area zinc oxide that is in the form of spheres or extrudates. Nominal size particles are in the range of 1/8" to 3/16" (+6-4 mesh screen).

The process is used primarily as a sulfur guard. It reduces H_2S in a process gas to a fractional ppm level before the gas is contacted with a sulfur-sensitive catalyst, such as the nickel catalyst used in methanation.

The zinc oxide adsorbent is discarded after it becomes loaded with sulfur, i.e., when a sulfur breakthrough greater than the permissible level takes place.

The overall chemical reaction occurring is:

$$ZnO + H_2S \longrightarrow ZnS + H_2O$$

It is more economical to use two beds of the zinc oxide adsorbent than one. (See Figure 3A.24-1.) The gas flow through the two-bed system is in series. When breakthrough occurs in the exit gas from the first bed, the first bed of adsorbent is saturated, but the second bed is capable of adsorbing more H_2S. At this point, the feed gas is diverted to what was formerly the second bed. The sulfur-loaded adsorbent in the first bed is then discarded and replaced with fresh adsorbent. The first bed then becomes the second bed. By alternating the beds in this way, it is possible to remove more sulfur for a given amount of zinc oxide adsorbent.

Operability Limits

Zinc oxide adsorbents are normally used in the temperature range of 660 to 840 °F at space velocities of 400 hour^{-1}. Temperatures down to 700 °F may be used, but the H_2S pickup is lower at low temperatures. They may be used at pressures ranging from atmospheric to over 50 atmospheres (720 psig). The space velocities may be increased as the H_2S concentration in the feed gas is decreased.

With a single bed operation, the zinc oxide adsorbent will contain 17 to 18 wt% sulfur before a sulfur breakthrough of 0.2 ppm H_2S in the exit gas occurs. With a two-bed operation, the sulfur loading can be increased to about 25 wt% of loaded adsorbent.

Purification Limits

Since a commercial coal conversion plant would generate hundreds of tons per day of sulfur equivalent in the raw gas, the amount of zinc oxide adsorbent required per day to remove all the sulfur would be prohibitively high. Therefore, this process would not be used to desulfurize the entire main gas stream. Instead, it would be used to remove the sulfur in a low H_2S content gas from a regenerable sulfur removal process, such as a Sulfiban, Stretford, or Benfield. It is possible to lower the H_2S concentration of the exit gas to a 0.02 ppm level, but a value of 0.2 to 0.5 ppm is more normal.

Mercaptans, if present in the feed gas, are removed at temperatures of 600 to 750 °F. Thiophenes are difficult to remove; about 60% are removed at temperatures around 750 °F. COS may be removed by this process but its presence reduces the capacity. It is advisable to hydrolyze COS to H_2S prior to zinc oxide adsorption.

Utility Requirements

Since the zinc oxide adsorbent is not regenerated, there are no major utility requirements. The feed gas to this process may require heating.

Environmental Considerations

The spent zinc oxide adsorbent contains ZnS. Spent zinc oxide adsorbent from a commercial coal conversion plant could be disposed of by landfill. In some cases, the amount of spent zinc oxide may be large enough to justify zinc recovery.

Remarks

Zinc oxide adsorbent can reduce the H_2S content of the feed gas to fractional ppm levels. It is not regenerable, and spent zinc oxide, containing ZnS, is disposed of by landfill. Zinc oxide is normally used as a guard to reduce the ppm level sulfur in the feed gas to a fractional ppm level.

References

1. Risenfeld, F. C., and Kohl, A. L., "Gas Purification," 2nd Edition, Gulf Publishing Co., Houston, Texas, 1974.

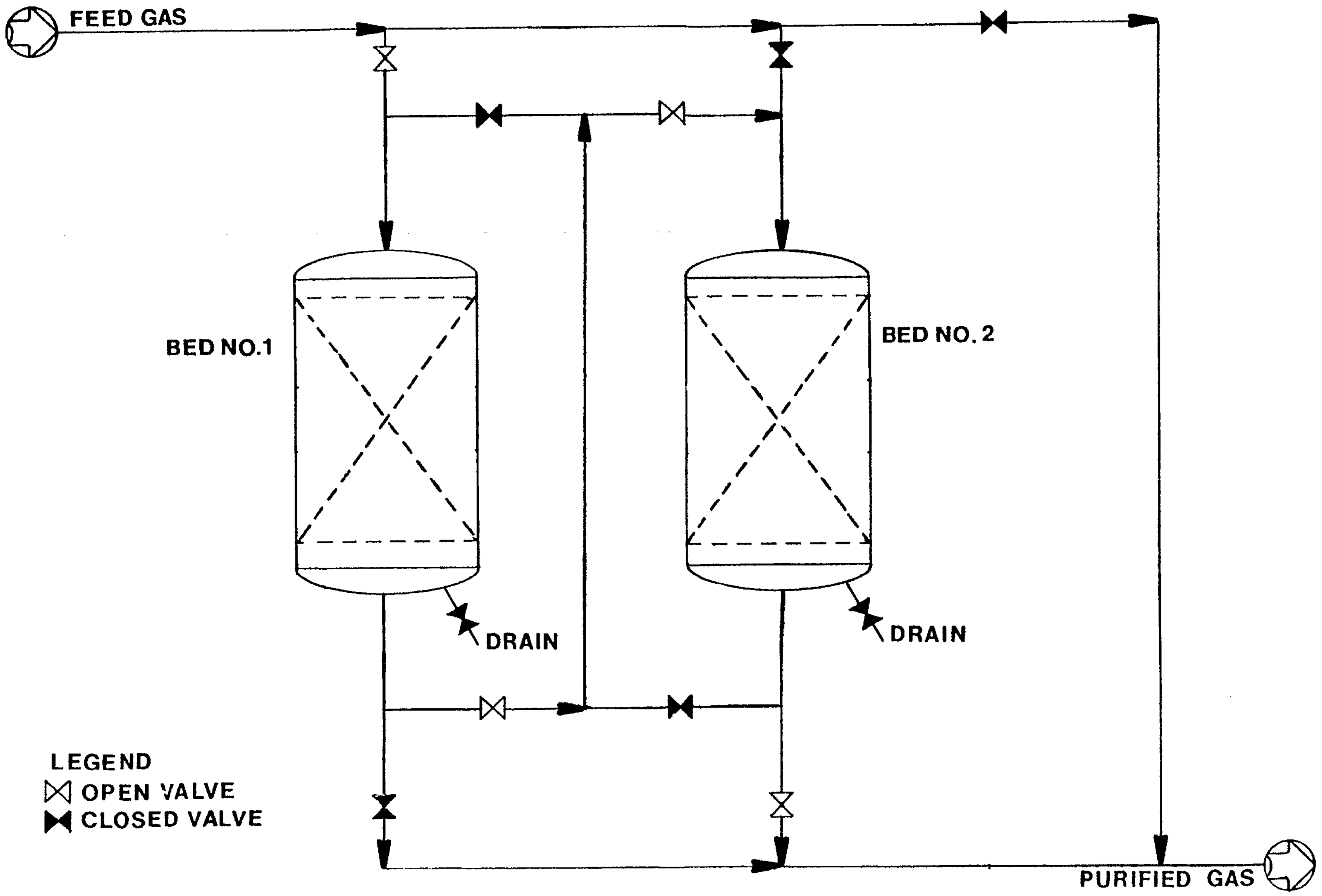

Figure 3A.24-1 Zinc Oxide Adsorption.

3B.1 CHEMIE LINZ/LURGI (CLL)

Licensor

Lurgi Kohle und Mineraloeltechnik GmbH
Bockenheimer Landstrasse 42
Postfach 119181, D-6000
Frankfurt am Main 1
West Germany

State of Development

This technology has been jointly developed by Chemie Linz AG and Lurgi, mainly for the removal of ammonia from the dephenolized gas liquor of the Lurgi gasifier and, in the case of coke oven plants, also the ammonia wash water. The ammonia product of the CLL is salable as ammonia of either agricultural or chemical grade.

Many plants that upgrade coal, such as coal gasification, carbonization, and coke oven plants, yield a gas condensate liquor carrying a high load of polluting substances that require treatment before discharge of the liquor to the environment. The output of gas condensate resulting from one ton of feed coal varies between 4.2 ft^3 (coke oven) and 42.3 ft^2 (pressurized coal gasification). The main harmful substances contained in these liquors may include suspended tars, oils and sediments, monovalent phenols (steam-volatile) and multivalent phenols, pyridine bases, ammonia, hydrogen sulfide, and hydrogen cyanide.

Because phenols act as a fish poison and, even in minute quantities, affect the taste of water, and ammonia promotes the eutrophication of water, processes for the removal of these substances were developed in the Ruhr District for several decades. After the phenol was removed by caustic soda to produce sodium phenolate, the ammonia was then removed by steam and processed into ammonium phosphate, a fertilizer.

When the market for ammonium phosphate fertilizer became practically nonexistent, means had to be found to recover the ammonia from gas condensate. To this end, Chemie Linz AG and Lurgi jointly developed the CLL Process, which permits the separate recovery of acid gases (CO_2 and H_2S) and ammonia from effluents by the use of stripping and scrubbing techniques and without the addition of chemicals or solvents.

Process Description[1 2]

The CLL process accepts dephenolized gas condensate, along with ammonia wash water in the case of coke oven plants, as shown in Figure 3B.1-1, and produces four effluent streams--(1) pressurized and ammonia-free acid gases (CO_2 and H_2S); (2) stripped gas condensate (water); (3) a small side stream of water and low-boiling point organic impurities (alcohols, ether, and ketones); and (4) pure liquid ammonia, either under pressure or at atmospheric pressure but cooled.

After heating, the dephenolized gas liquor enters the deacidifier, where the remaining gases and any remaining dephenolizing solvent are stripped out by reboiler steam. The gases leaving the stripper are scrubbed with cooled waste water under elevated pressure to remove ammonia. The stripped gases are sent back to the phenol recovery unit from which the dephenolized gas liquor originally came. The gas liquor containing the ammonia leaves the bottom of the deacidifier and is pumped, after cooling, to a total stripper, where all the ammonia and the remaining gases are stripped out by reboiler steam at near atmospheric pressure.

The bottom product of the total stripper is the clean gas liquor (water) containing less than 100 ppm ammonia. This water is sent after cooling to wastewater treatment for final treating.

The overhead vapors from the total stripper are partially condensed in the bottom of the acid gas (CO_2) scrubber to increase the ammonia concentration. The condensate is refluxed back to the total stripper.

In the acid gas scrubber, the vapors are scrubbed by a recycled aqueous ammonia solution from the process. The heats of reaction and condensation are recovered by cooled pump-arounds.

The bottom stream of the acid gas scrubber, which contains ammonia and ammonium salts, is pumped to the ammonia stripper. The bottoms of the ammonia stripper, containing a highly concentrated ammonium salt solution, is recycled back to the deacidifier.

The ammonia vapors in the acid gas exiting from top of the scrubber must be dried and subjected to fine purification. These vapors can also contain low-boiling organic matters, such as acetone. They are therefore compressed in the first stage of a compressor and washed with liquid ammonia in a drying column. This washing process dehydrates the gases and at the same time removes the organic components, which are withdrawn from the column bottom, together with water, and sent to the wastewater stream. The ammonia recycle for the acid gas scrubber is withdrawn as a side stream from the dehydration column.

In the following compressor stages, the ammonia vapors are compressed to a point where they can be condensed either with cooling brine or cooling water. Assuming a condensation temperature of about 104 °F, corresponding to, for instance, a maximum cooling water supply temperature of about 77 °F, the ammonia vapors must be compressed to about 216 psig.

As an alternative, condensation can be accomplished by absorption in water and stripping at elevated pressure. The maintenance work for the machines is no doubt less in this case compared to condensation by direct compression, which is the more elegant solution.

Chemical Description[1 2]

Other than the input gas liquor and water, no chemicals are added to the CLL to strip and scrub the input material into four by-product/water streams. Separation of components is accomplished by using pressure and temperature control to vary the kinetic parameters.

The acid gas components, carbon dioxide and hydrogen sulfide, are separated from ammonia by distillation only, using pressure to take advantage of the maximum temperature azeotropes (boiling properties) of the substances. The acid gases are stripped with steam overhead and freed of residual ammonia by washing with cold water in the pressurized deacidifier.

To ensure simple and smooth operation of stepwise condensation, particular care has to be applied when designing the plant because the prevailing temperatures and concentrations create the hazard of the formation of solid ammonium salts.

Operability Limits[1 2]

The pressure in the CLL process varies from near atmospheric in the total stripper to an optimally set value in the deacidifier in accordance with the carbon dioxide and ammonia content. Operating pressures and temperatures are proprietary, but it is known that acid gas (CO_2 and H_2S) effluent is under a pressure of about 58 psig and is cooled to about 104 °F.

The ammonia coming from the NH_3 condensor at 104 °F must be compressed to 216 psig. Significantly higher pressures are required to strip the ammonia by absorption in water.

Purification Limits[1]

The overhead vapor from the acid gas (CO_2) scrubber consists of ammonia containing about 4% water, less than 1% CO_2, and less than 1 ppm H_2S. The stripped gas condensate (water) from the total stripper contains less than 100 ppm ammonia. The liquid ammonia is salable as chemical or agricultural grade.

Utility Requirements

The utility requirements for the proprietary CLL system are not available.

Environmental Considerations

The acid gases require further processing in a sulfur recovery unit. Stripped gas condensate (water), which has less than 100 ppm of ammonia, is suitable for further biological processing. The low-boiling point organic impurities, which include alcohols, ether, and ketones, can be burnt or blended into other waste streams. The disposition of each waste product must be determined for each plant application and location.

Remarks

The high purity of the ammonia product, particularly its freedom from H_2S and CO_2, makes it suitable for fertilizer production and for metallurgical purposes, for instance in bright annealing furnaces or for the gas nitriding of steels. Steel mills having their own coke oven plants are well suited for the CLL process.

Outside the Ruhr District, the transport costs of caustic soda solution and sodium phenolate were not acceptable, so during the late 1930s Lurgi developed the Phenosolvan process (see Chapter 3C.3), which is used for direct recovery of oxide phenol and for treatment of effluents from carbonization and coal gasification plants. An improved version of the Phenosolvan process has been recently combined with the CLL process. This eliminated the need for intermediate storage tanks and other equipment, such as equipment for solvent stripping in the gas cycle, that is used in the Phenosolvan process when it is run separately. In many applications, however, the CLL process is used as a separate unit from the Phenosolvan process.

References

1. Woehler, F., Dr., "Removal and Recovery of Phenol and Ammonia from Gas Liquor," undated report from Lurgi Kohle and Mineraloetechnik GmbH, Frankfurt/-Main, West Germany, released during or after 1977.

2. Schreiner, M., "Research Guidance Studies to Assess Gasoline from Coal by Methanol-to-Gasoline and Sasol-Type Fischer-Tropsch Technologies," Mobil Research and Development Corp. report to U. S. Department of Energy under Contract No. EF-76-C-01-2447, DOE report No. FE-2447-13, August 1978.

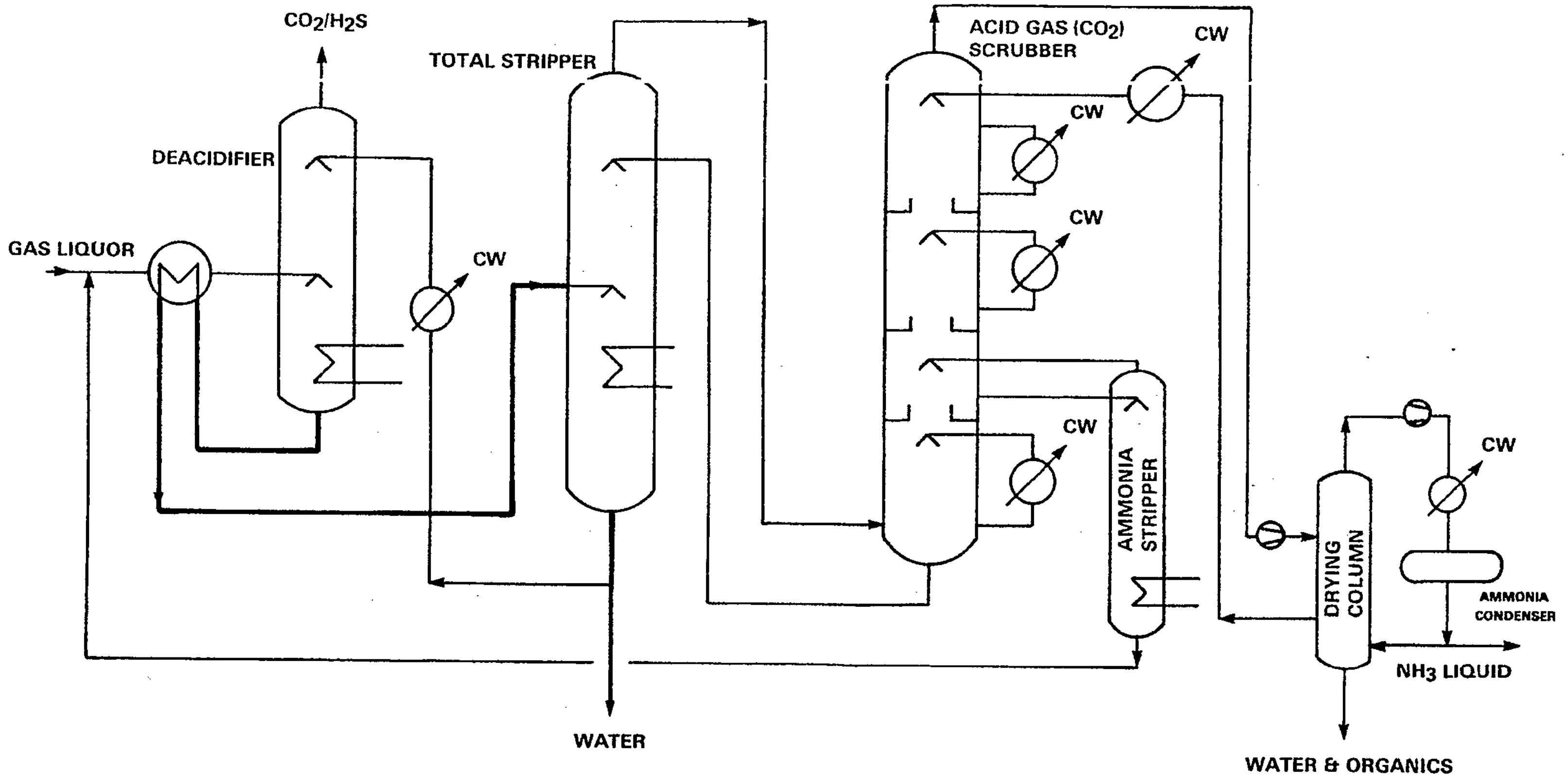

Figure 3B.1-1 -Chemie Linz/Lurgi (CLL) Process.

3B.2 CHEVRON WASTEWATER TREATING (WWT)

Licensor

Chevron Research Company
525 Market Street
San Francisco, California 94105

State of Development

The Chevron Wastewater Treating (WWT) process is a commercially used, patented process for treating sour water streams generated by petroleum refineries, coal processing and gasification plants, and synthetic fuel plants. First onstream use was at a Chevron plant in Richmond, California in 1966. Twenty-four plants including 12 Chevron plants have been installed. Most of these have 200 to 300 gpm capacity. One unit, Getty Refining, has a 1400 gpm capacity.[1]

Process Description[1]

The Chevron WWT process recovers high purity ammonia and hydrogen sulfide while producing clean water suitable for reuse or discharge. (See Figure 3B.2-1.) The H_2S is produced as a gas suitable for feed to a sulfur recovery unit.

The WWT process consists of three main processing steps: (1) degassing and feed storage, (2) acid gas (H_2S and CO_2) stripping, and (3) NH_3 stripping and purification.

Sour water feed is combined with a recycle stream from the ammonia stripper, cooled, and passed through a degasser, where dissolved hydrogen, methane, and other light hydrocarbons are removed. The recycle stream is rich in ammonia, which helps keep acid gases in solution in the degasser, thereby minimizing release of acid gas. The degassed sour water is pumped to an offplot storage tank to adjust flow rates and composition changes while also providing the opportunity to remove entrained oil and solids.

From the feed tank, the degassed sour water feed is pumped to the WWT unit, where it is heated by feed-bottoms exchange and then fed to the acid gas stripper. The H_2S stripper is a steam reboiled distillation column. H_2S and CO_2 are stripped overhead, and the resulting gas is water washed to remove residual ammonia.

The H_2S stripper bottoms, which contains NH_3 and some acid gases, is fed directly to the NH_3 stripper, which is a steam reboiled, refluxed distillation column. Clean water bottoms contains less than 50 ppm of free NH_3 and less than 5 ppm of free H_2S. (In the event that the feed contains acids that "fix" NH_3 as an acid salt, technology is available to remove this impediment to NH_3 stripping.)

The NH_3, H_2S, and CO_2 stripped from the water in the NH_3 stripper are passed through an overhead condenser and recovered as a vapor and liquid. The liquid is used as column reflux, and the vapor (when recovered) is passed through a two-stage scrubbing system to remove acid gas. The H_2S content of the ammonia is typically less than 5 ppm.

Chemical Description

The process uses normal physical solubility criteria, which are a function of temperature and pressure.

Operability Limits

Nominal pressure and temperature used are 100 psig and 200 °F, respectively.

Purification Limits[1]

The process produces ammonia stream with 5 ppm H_2S. It also produces effluent water with 50 ppm free NH_3 and 5 ppm H_2S.

Utility Requirements

Steam: Not Available
Cooling water: Not Available

Environmental Considerations[1]

The effluent water stream contains less than 50 ppm free NH_3 and 5 ppm H_2S.

Remarks

The WWT process has been used in a number of different applications. Its operating parameters are known and thus can be compared against an alternate choice for the purpose of selection.

Reference

1. Chevron Research Co., "Chevron Waste Water Treating (WWT) Process," May 23, 1979.

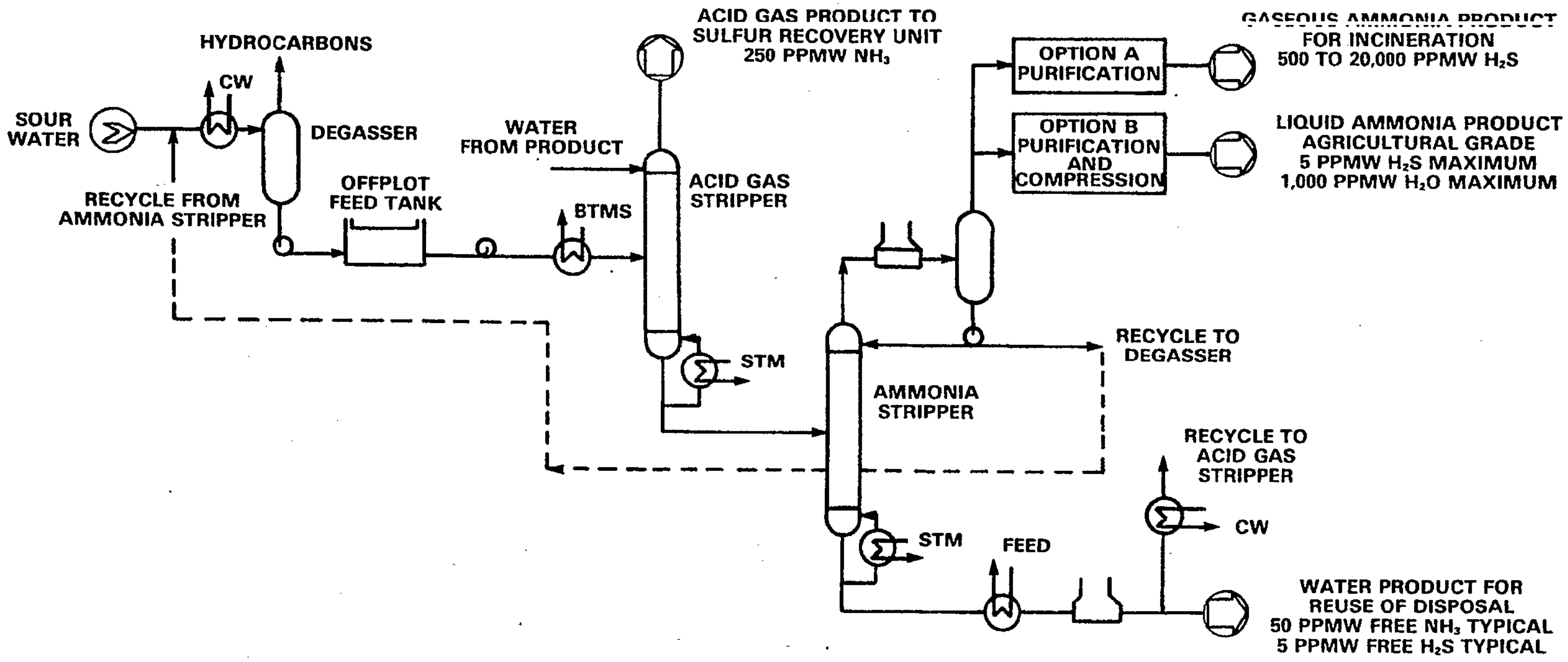

Figure 3B.2-1 Chevron WWT Process.

3B.3 USS PHOSAM-W

Licensor

USS Engineers and Consultants, Inc. (UEC)
600 Grant Street
Pittsburgh, PA 15230

State of Development

The USS PHOSAM-W Process is the application of PHOSAM technology to coal gasification, coal liquefaction, and other energy and chemical processes outside the coke-oven field. The PHOSAM process was developed in the late 1950s by U. S. Steel Corporation's Research Laboratory to recover ammonia from coke-oven gas and gas liquors as a high quality anhydrous ammonia.[1] The process has been in successful operation at U. S. Steel's largest coke plant since 1968. There were 18 PHOSAM and PHOSAM-W plants in operation worldwide as of mid 1981.

The PHOSAM W technology can be used for the recovery of ammonia from any gas or vapor stream and is particularly advantageous when CO_2, H_2S, and other acidic gases are present.[2] The PHOSAM-W process has been selected and licensed for the proposed coal gasification projects in North Dakota, Wyoming, Texas, Illinois, and Ohio and for shale oil in Colorado.[3]

Process Description[1]

One arragement of the PHOSAM-W process is shown schematically in Figure 3B.3-1. In this arrangement, the feed stream is ammonia-bearing process condensate and other contaminated waters from the coal gasification process. The water, which has been preheated in the lean solution cooler, is stripped of its free ammonia and acid gases in the sour water stripper, using direct or indirect low-pressure steam. The vapor passes into the bottom of the ammonia absorber, where its ammonia is removed by countercurrent contact with ammonia-lean PHOSAM solution entering at the top.

Alternatively, the feed may be vapor from one or more separate strippers, or an ammonia-bearing process gas, either of which can be introduced directly into the absorber. Ammonia-free gas and water vapor leave the top of the absorber and may be passed through a partial condenser if desired.

Ammonia-rich PHOSAM solution is pumped from the bottom of the absorber and heated by interchange with hot lean solution. It then flows to a contactor, where the small quantities of acidic gas dissolved in the rich solution are removed and recycled to the absorber. In certain cases, the contactor may be combined with the absorber.

The rich solution, purged of acid gases, is pumped from the contactor to an interchanger and further heated with the overhead vapors from the stripper. It then enters the top of the stripper, where NH_3 is stripped from the rich solution at elevated pressure by live steam entering the bottom of the column. Alternatively, a reboiler may be used with high-pressure steam, and the steam condensate recovered.

Lean solution leaving the stripper bottom is cooled by exchange with the rich solution from the absorber. It is further cooled (in the feed water preheater) and recycled to the top of the absorber to continue the process.

Aqua-ammonia vapor from the top of the stripper condenses in the two-stage condenser and flows to the fractionator feed tank. From here, the aqua-ammonia is pumped into the ammonia fractionator, where it is distilled at elevated pressure into a high-purity NH_3 vapor in the overhead and a water stream containing less than 0.05% NH_3 in the bottoms. Steam enters at the base of the column and provides the necessary vapor flow for stripping and rectifying the NH_3. Alternatively, the vapor may be generated in a reboiler. The overhead, pure NH_3 vapor, is condensed to form reflux and the product anhydrous liquid ammonia.

A small amount of sodium hydroxide solution is metered into the fractionator system to prevent the accumulation of acid gases. The fractionator bottoms contain recoverable heat and traces of free alkali. It may be recycled to the sour water stripper or flashed separately. In either case, it provides some of the stripping steam required.

Chemical Description[4]

The absorbent liquid contains ammonia and phosporic acid of the general formula $(NH_4)_nH_{3-n}PO_4$. When n is lower than 1.5, the solution is considered lean in ammonia, while values above 1.5 are characteristic of rich solutions. The licensor varies the n values of rich and lean solutions in designing for specific requirements. The absorption reaction is exemplified as follows:

$$(NH_4)_{1.3}H_{1.7}PO_4 + 1/2NH_3 \longleftrightarrow (NH_4)_{1.8}H_{1.2}PO_4$$

Operability Limits

In coke-oven plants, the PHOSAM technology is used to remove and recover ammonia from coke-oven gas, from sour water stripper vapors, and from mixtures of the two. These systems contain CO_2, CO, CH_4, H_2, H_2S, HCN, phenolics, aromatics, olefins, and tarry matter. The process achieves, typically, 99.7% recovery of the available ammonia as commercially salable grade and is capable of producing 99.99% purity ammonia.

In PHOSAM-W applications, ammonia absorption is generally performed on vapor streams at absorption temperatures up to 210 °F (as compared to coke oven gas absorption at 105-140 °F). At the higher temperatures, absorption efficiencies in the range of 96-99.5% are obtained. However, the increased ammonia slippage resulting from higher absorber temperature can be eliminated by an after cooler that produces a condensate containing the ammonia, which is recycled to the sour water stripper.

The PHOSAM-W process employs a chemisorption system to absorb the ammonia selectively in the presense of other chemical species. It does not rely on relative volatility differences as would a distillation process and thus is claimed to be relatively immune to upset and to uncertainties in the feed composition.

Stripping of the rich solution and fractionation of the aqua-ammonia are carried out at 180 to 250 psig pressure using direct or indirect steam. The steam consumption in the stripper is increased as the stripper pressure is decreased. Design techniques have been developed to permit satisfactory application of the PHOSAM-W process to liquid, vapor, and gaseous streams of markedly different compositions.

Purification Limits

The free ammonia content of waste waters can be reduced to 50-200 ppm or lower if required.

The PHOSAM-W Process deals with free ammonia only, but the licensor reports that its USS CYAM System may be advantageously combined with PHOSAM-W where fixed ammonia must also be removed from the wastewater. The CYAM System is claimed to produce low cyanide as well as low ammonia effluents and to enable the use of either NaOH or low-cost lime to release the fixed ammonia.[5]

The anhydrous ammonia recovered is of salable commercial/agricultural grade.

Utility Requirements

Utility requirements for the PHOSAM-W process depend on the type of feedstream, whether a wastewater stripper is included, and specific design paramaters, such as steam pressure available, condensate recovery requirements, etc.

Utility requirements for a typical PHOSAM-W plant, including wastewater stripping, are as follows[pc]

Steam @ 550 psig, lb/lb of NH_3	12
Steam @ 25 psig, lb/lb of NH_3	8
Cooling Water, gal/lb of NH_3 (reducible with air coolers)	30
Electrical Power, kWh/lb of NH_3	0.02
Chemicals	
H_3PO_4 Makeup (as 100% H_3PO_4), lb/lb of NH_3	0.002
NaOH (as 100% NaOH), lb/lb of NH_3	0.003

Environmental Considerations

The wastewater leaving the bottom of the fractionator will contain various sodium salts and some free caustic. It may be combined with the stripped wastewater and used for cooling tower makeup, or used for ash quenching, or treated and discharged.

Remarks

The PHOSAM-W Process is a chemisorption process. It operates on liquid, gas, or vapor feeds with relatively low ammonia concentrations.

References

1. "U.S. Steel PHOSAM Process - Recovery of Anhydrous Ammonia," USS Engineers and Consultants, Inc., Bulletin No. 2-01.
2. Hamilton, C. W. and Rice R. D., "New Developments in the USS PHOSAM Process," presented at the 34th Ironmaking Conference, American Institute of Mechanical Engineers, Toronto, Canada, April 1975.
3. "USS PHOSAM-W Process," a Bulletin by USS Engineers and Consultants, Inc.
4. Riesenfeld, F. C., and Kohl, A. L., "Gas Purification," Gulf Publishing Company, Houston, Texas, 1974.
5. "U.S. Steel CYAM System - For Removal of Ammonia, Hydrogen, Hydrogen Cyanide, and other Acid Gases from Aqueous Streams," USS Engineers and Consultants, Inc., Bulletin No. 2-08.

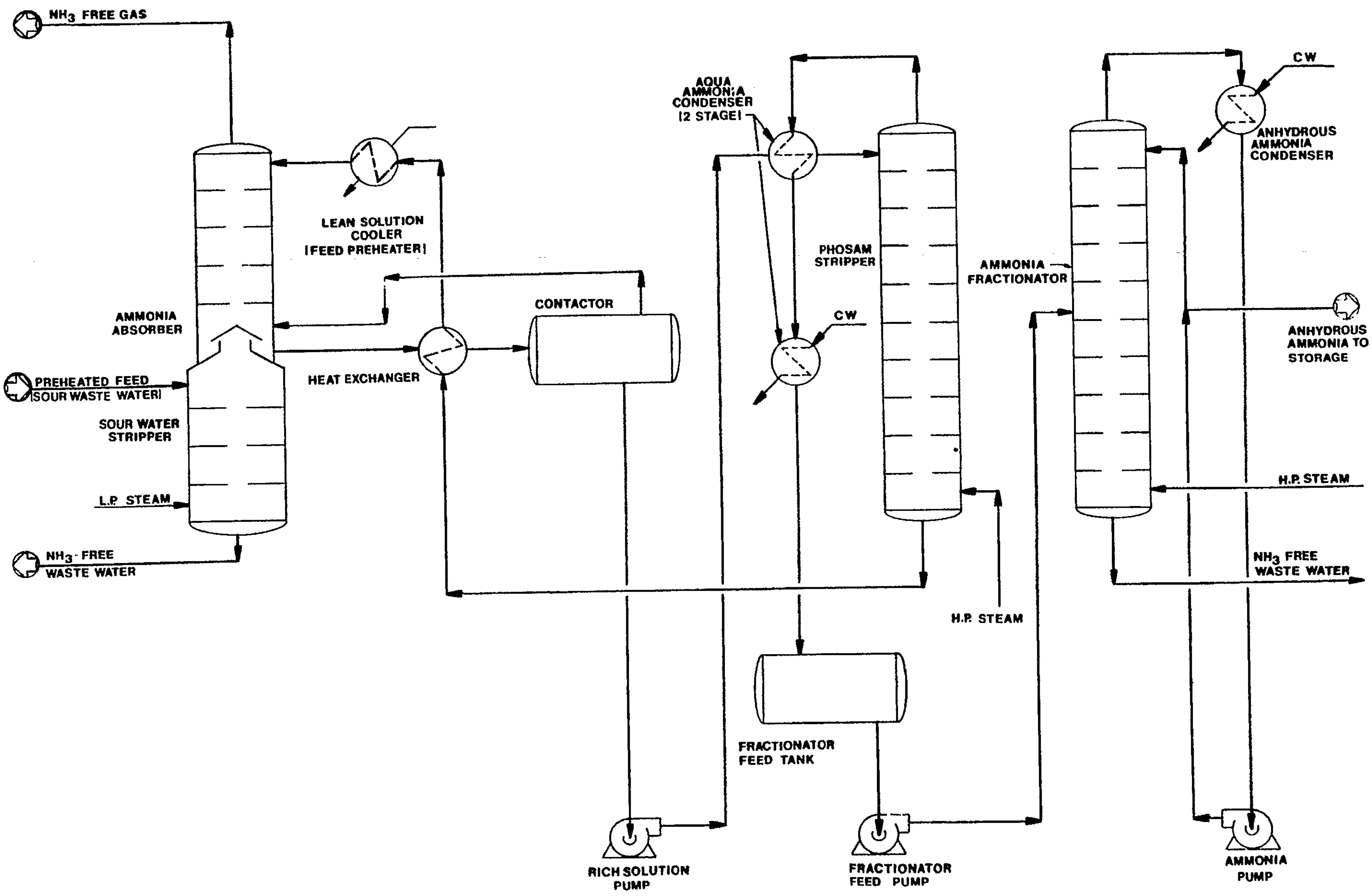

Figure 3B.3-1 USS PHOSAM W Process.

3C.1 BIODEGRADATION FOR PHENOL REMOVAL

Licensors

The Biodegradation or the activated sludge process for wastewater treatment for the removal of organics is offered by many companies, such as Suntech, Lotepro, and others. The process described here is the UNOX System licensed by

Lotepro Corporation
1140 Avenue of Americas
New York, New York 10036

State of Development

The UNOX system oxygen activated sludge process for secondary biochemical treatment of wastewater was developed by Union Carbide in the late 1960s and commercially introduced in early 1970. By early 1977, there were 63 UNOX Systems operating.[1] In addition, another 67 UNOX Systems were under construction and more than 90 were in the design stage. This technology was acquired by Lotepro in 1980.

Process Description[1, 2]

The UNOX System uses high-purity oxygen instead of air to supply oxygen to the microorganisms that metabolize organic materials in municipal and industrial wastewaters through a biochemical oxidation process. This process (Figure 3C.1-1) effectively removes the wastewater components that produce an undesirable biochemical oxygen demand in receiving waters and eventually result in pollution. A high level of dissolved oxygen in activated sludge mixed liquor has many beneficial effects on the microorganisms that metabolize the wastes. Increases in dissolved oxygen concentrations produce increased sludge settling rates, improved sludge dewatering characteristics, and a more concentrated, smaller volume of sludge to be disposed of.

The basic elements of a typical UNOX process using surface aerators are contained in a three-stage oxygen-activated sludge system. The three tanks are separated by baffles, and each tank has a surface aerator, as shown in the figure.

Chemical Description

In activated sludge processes, the bacteria use noxious compounds, such as phenol, as their source of food, and produce carbon dioxide and water as the end products. The bacteria are aerobic: that is, they require oxygen to live, and each reaction in this scheme is performed by a specific enzyme. These organisms are not solely restricted to phenol destruction but may also readily feed on other phenolic type compounds, such as cresols, as well as most other organic compounds, including acids, aldehydes, and alcohols. The nitrogen and sulfur compounds are treated by bacteria. The nitrifying bacteria produce the following reactions:

$$NH_3 + \text{oxygen} \xrightarrow{\text{Nitrosomonas}} NO_2^- \text{ (nitrite)} + \text{energy}$$

$$NO_2^- \text{ (nitrate)} + \text{oxygen} \xrightarrow{\text{Nitrobacter}} NO_3^- \text{ (nitrate)} + \text{energy}$$

Autotrophic sulfur bacteria perform the following reaction:

$$H_2S + \text{oxygen} \xrightarrow{\text{Thiobacillus}} H_2SO_4 + \text{energy}$$

Operability Limits[3]

Typical operating conditions for activated sludge processes include a bacterial sludge volume index of 4 to 6 percent, a temperature range of 70 to 85 °F, and a pH range of 6.0 to 9.0. The processes will operate with a temperature as low as 60 °F and as high as 100 °F. Other limits are dissolved and emulsified oil concentrations as high as 150 ppm, phenol concentrations up to 200 ppm, and sulfide concentrations up to 50 ppm. Typical range of phenol removal is 90 to 99%. It is important to avoid sudden or shock loadings. Typical range of phenol removal is 90 to 99%. The presence of heavy metals can have an adverse effect on the efficiency of the biological oxidation process, particularly if a rapid change in their concentration occurs. Nitrogen and phosphorus must be present in the waste stream to keep phenol oxidation at its optimum level.

Utility Requirements

The utility requirements vary with each application.

Environmental Considerations

Because the effluent water quality is high, further treatment is not necessary, and the effluent may be discharged to rivers and streams.

Remarks

The activated sludge process has advantages over chemical treating and incineration. The use of sludge recirculation in the aeration basin for the metabolic oxidation of excess bacterial growth eliminates need for separate digestion equipment. The process is highly sensitive to pH levels, presence of heavy metals, and oxygen supply.

References

1. Union Carbide, "UNOX System," Wastewater Treatment, Bulletin F-4107.
2. "Environmental Assessment Data Base for Low/Medium Btu Gasification Technology," Vol. II, EPA-600/7-77-125b, November 1977.
3. Elkin, H.F., "Activated Sludge Process Application to Refinery Effluent Water," Sewage and Industrial Waste, Vol. 28, No. 9, September 1956.

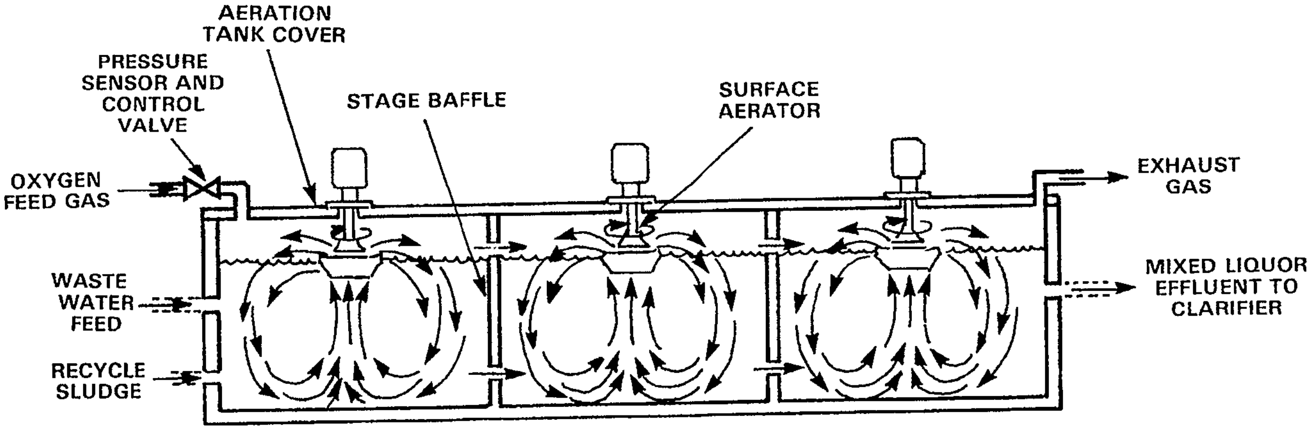

Figure 3C.1-1 UNOX Biological Degradation Process.

3C.2 CHEM-PRO PHENOL RECOVERY

Licensor

Chem-Pro Equipment Corporation
P.O. Box 1248
Fairfield, NJ 07006

State of Development

The Chem-Pro process was developed by J & L Steel Co. and licensed to Chem-Pro Equipment Corporation for recovery of phenol from waste waters by liquid-liquid extraction. The process uses a proprietary immiscible solvent to extract phenols from a wide range of aqueous wastes. One plant has been in operation for over 15 years, and another has recently gone on stream. Designs are being prepared to adapt the process to two other plants.[1]

Process Description[1, 2]

Figure 3C.2-1 shows the Chem-Pro process. The phenol extraction is carried out in a multistage reciprocating plate extraction column. A proprietary solvent is used in this column to extract the phenols from the wastewater stream. The extract, containing the solvent and the phenols, is sent to a distillation column to separate the phenols from the solvent. The solvent is recovered from the top of the distillation column and is recycled back to the extraction column. The phenols stream from the bottom of the distillation column is cooled and pumped to storage.

The wastewater leaving the extraction column is saturated with solvent. This solvent is recovered by stripping it with steam in a stripper column. The recovered solvent is then recycled to the extraction column.

Chemical Description

The Chem-Pro process uses a proprietary solvent to extract phenols from the aqueous streams. Extraction is a physical process, and no chemical reaction occurs. The difference in concentration between the aqueous stream and the immiscible solvent results in mass transfer of phenols to the solvent.

Operability Limits[2]

The extraction process can handle incoming phenol concentrations of from a few hundred parts per million to saturation (8%). It can process all concentrations encountered in industrial situations and recovers a dry phenolic product.

Purification Limits[1]

Raffinate (aqueous dephenolized waste) phenol concentrations of less than 1.0 ppm have been demonstrated.

Utility Requirements

The typical requirements for 99.7% phenol recovery at an influent feed rate of 1000 lb/hr with a phenol concentration of 0.5% are

Steam, lb/hr	60.00
Cooling Water (87 °F - 105 °F), gpm	3.24
Electric Power (480v, 30 , 60 Hz), kWh	0.81

Environmental Considerations

The concentration of phenol in the effluent ranges from 1 to 4 ppm, and that in the recycle solvent is 1 ppm. This is within the environmental guidelines and requires no further processing.

Remarks

The process is applicable to most aqueous streams containing phenol, substituted phenols, cresols, substituted cresols, dihydric phenols, and trihydric phenols. Applications have included aqueous distillate generated during the manufacture of phenol resins, coke plant weak ammonia liquors, and coal gasification and liquefaction aqueous wastes.

References

1. "Extraction Process Recovers Phenols from Waste Streams," Chemical Processing, 1978.
2. Lorton, G. A., "Removal of Phenols from Process Condensate," Interim Report, C. F. Braun & Co., October 1977.

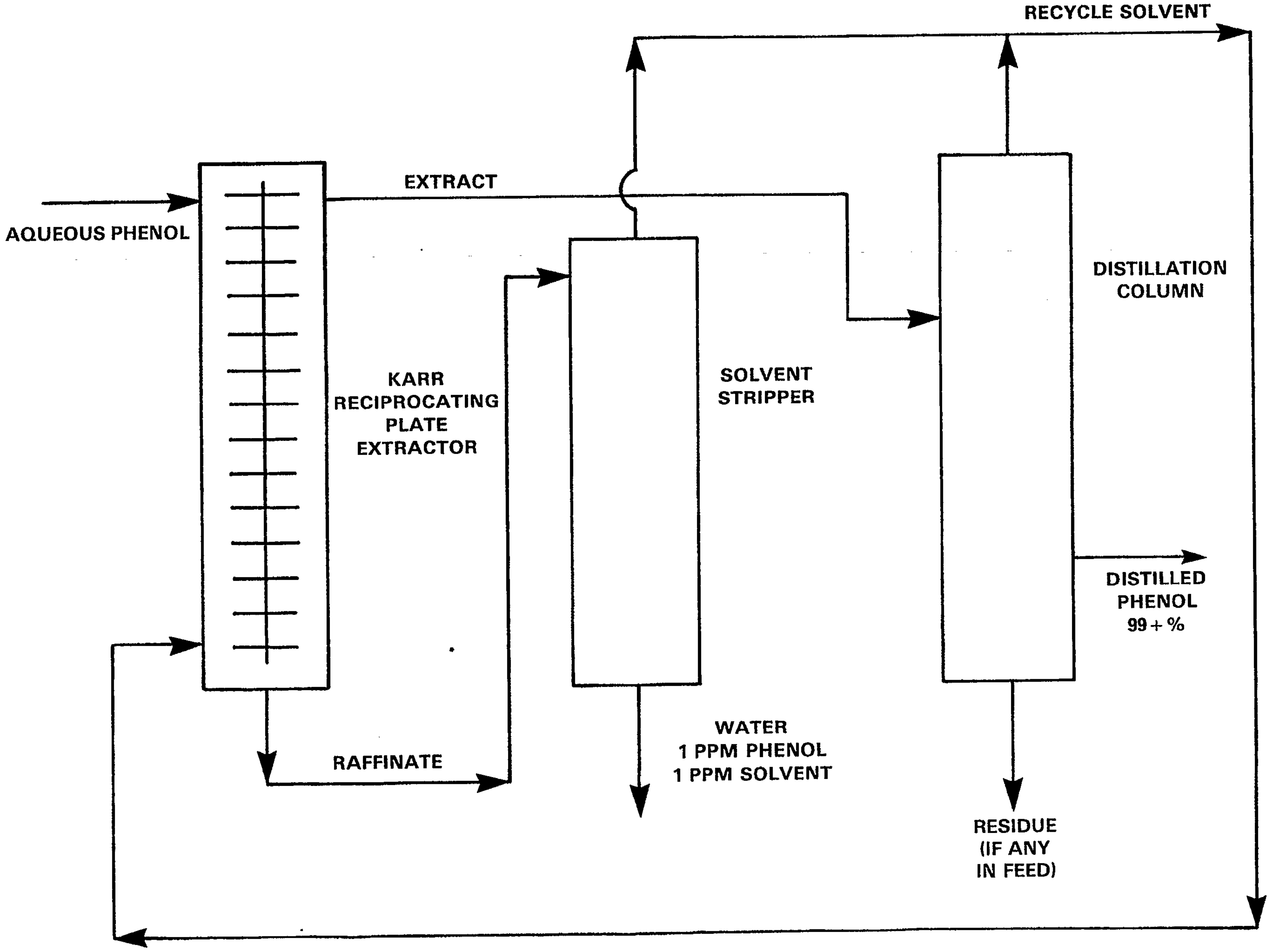

Figure 3C.2-1 Chem-Pro Phenol Recovery Process.

3C.3 PHENOSOLVAN

Licensor

Lurgi Kohle und Mineraloeltechnik GmbH
Bockenheimer Landstrasse 42
Postfach 119181, D-6000
Frankfurt Am Main 1
West Germany

State of Development

Thirty-two commercial installations have been made since 1940. The process is being used in coal gasification facilities in Sasolburg, South Africa (Sasol), and Kosovo, Yugoslavia.[1]

Process Description[2]

Figure 3C.3-1 represents the flow scheme of the Phenosolvan process. This process extracts the phenols out of the feed stream into the extracting agent, or solvent. The feed stream is first filtered to remove the suspended matter and then cooled. It then enters a multi-stage countercurrent extractor in which a light aromatic oil (solvent) is used to extract the phenols. The nature of the solvent may vary with the application. Examples are butyl acetate (being used at Sasol) and isopropyl ether. The extract leaving the tower is then sent to a distillation column, where phenols are separated from the solvent. The solvent is recycled to the extractor. The extracted water, which is full of phenols but still contains a small amount of solvent, is preheated and freed of solvent in a desorption column by circulating stripping gas.

The entrained solvent is recovered from the stripping gas by washing with crude phenol. The solvent, containing crude phenol, is passed to the extract distillation column.

Chemical Description

Liquid-liquid extraction as employed in the Phenosolvan process is a physical mass transport phenomena, and no chemical reaction takes place. The solubility of the phenols is greater in the solvent than in the water. A preferential dissolution of phenols in the solvent takes place when the two streams come into contact.

Operability Limits[2]

The process operates at atmospheric pressure and temperatures below the solvent boiling point. The operating temperature at the Sasol coal liquefaction plant is 158 °F.

Purification Limits[2]

In general, the process accomplishes 99% removal of monohydric phenols, 60.0% removal of polyhydric phenols, and 15.0% removal of other organics. Approximately 95% total organics are removed at the Sasol coal liquefaction facility.

Utility Requirements

Steam, lb/gal feed = 0.08 to 0.27
Cooling water, gal/gal feed = 1.5
Electric power, kWh/gal feed = 0.004 to 0.006

Environmental Considerations

Dephenolized liquor, the effluent wastewater, contains traces of phenols, solvent, other dissolved organics, and dissolved acid gases. Although the wastewater has had the bulk of the dissolved phenols removed from it, the resulting effluent still requires the use of a polishing process, such as carbon adsorption, biological oxidation, or cooling tower air stripping. The effluent may also contain significant amounts of dissolved acid gases that will require further treatment.

Remarks

The process solvent must have relatively low volatility, low solubility in water, and high distribution coefficient. Solvents, such as isopropyl ether with a flash point of 15 °F, must be handled very carefully.

References

1. Lurgi Brochure, "Upgrading of Solid Fuels."
2. Cavanaugh, E. C., and Corbett, W. E., "Environmental Assessment Data Base for Low-Medium - BTU Gasification Technology," EPA-600/7-77-125b, Radian Corp., November 1977.

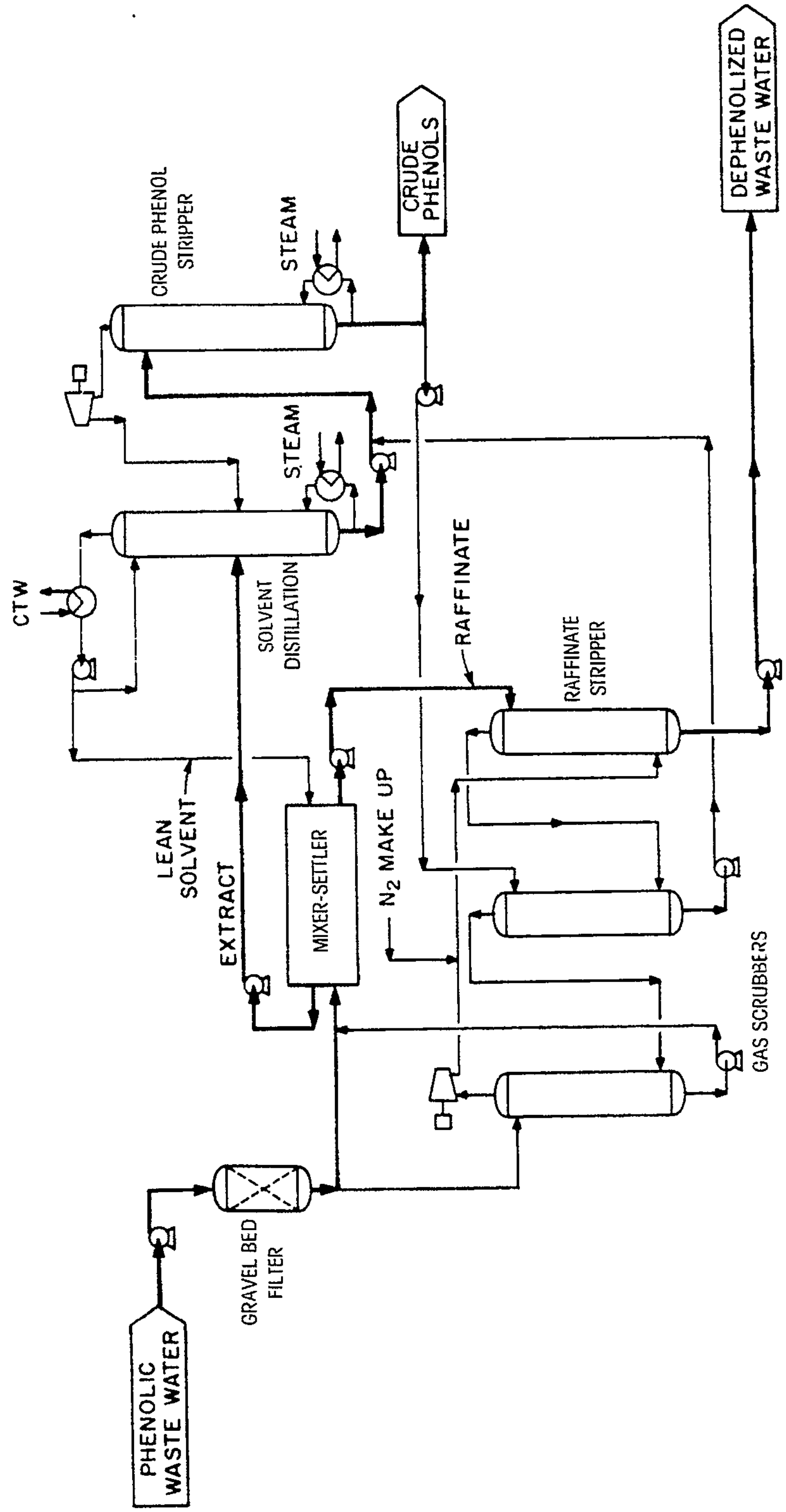

Figure 3C.3-1 Phenosolvan Process (Reference 1)

3C.4 ROHM AND HAAS PHENOL RECOVERY

Licensor

Rohm and Haas Company
Independent Mall West
Philadelphia, PA 19105

State of Development[1] [2]

This phenol recovery process was developed by the Rohm and Haas company for removal and recovery of phenolic compounds from aqueous streams by adsorption on a porous organic resin. The process has been applied to the treatment of effluent from plants manufacturing and using phenol and phenolic compounds. Examples are plants manufacturing pesticides Parathion and phenoxy acids, certain phenolic resins, and sour water from oil refineries. The process is also used to purify waste streams by selectively removing the organics. Polymeric adsorption, the regeneration of the adsorbent by acetone, and phenol recovery have been commercially proven at two chemical processing plants.

Process Description[1] [3]

A flow diagram of the Rohm and Haas process is illustrated in Figure 3C.4-1. The process uses high surface adsorbent resins called Amberlite. These resins are in the form of hard insoluble beads of porous crosslinked polymer with no ionically functional sites.

This process is cyclic in nature and consists of three steps: loading; regeneration and rinse; and distillation and separation.

Loading: Adsorption is normally carried out in two columns, each containing a bed of adsorptive resin; one is in the loading step while the other is under regeneration. Loading is performed at a space velocity (i.e., volumetric flow rate per volume adsorbent) dependent on the phenol concentration of the influent, the desired effluent quality, and the time required to regenerate the unit.

Regeneration and Rinse: The beds are regenerated by desorbing the phenolics from the resin with a solvent (acetone). Following regeneration, solvent in the beds is displaced from the adsorbent by water or steam. The solvent-phenolic-water mixture from the regeneration and the solvent-water mixture from the rinsing steps are distilled to recover the solvent. Often, part of the spent regenerant is used twice to insure the highest phenolic concentration possible.

Distillation and Separation: The distillation section permits solvent recovery at high purity, leaving water and phenolics in the bottom of the fractionation column. The acetone from the overhead of the fractionator is recovered and stored for reuse during the regeneration step. The phenol and water leave the bottom of the fractionator and are cooled and decanted in the separator. The phenol-rich stream is pumped to storage.

Chemical Description

The Rohm and Haas process uses Amberlite polymeric adsorbents to remove phenolics from aqueous waste stream. The most significant feature of Amberlite adsorbents is the nature of their different surfaces. The phenomenon of adsorption involves binding the sorbate (material to be adsorbed) to a solid surface. Phenol, being a moderately polar molecule, can be adsorbed by Amberlite XAD-4. The adsorption can take place either from aqueous or nonaqueous systems. The adsorption from water takes place by association with the hydrophobic benzene ring. Adsorption, a physical process, can be reversed by regenerating the bed with acetone.[4]

Operability Limits

Phenol, a moderately polar molecule, can be adsorbed from both the aqueous and nonaqueous media. For desorption, some of the adsorbents will withstand temperature of 400 °F. Caustic, acetone, and methanol can be used for regeneration, depending on the origin of the phenolic effluent.

Purification Limit

The process will reduce the phenolics in the treated effluent to less than 10 ppm. A level of less than 1 ppm phenolics can be achieved in many cases.

Utility Requirements

Utility requirements for this process are not available.

Environmental Considerations

The phenolic content of the treated effluent is well within the environmental standard of 10 ppm. The regenerant content may or may not require additional treatment, depending on the reuse of the treated effluent.

Remarks

Rohm and Haas' Amberlite resins are commercially proven adsorbents that yield high purity effluent. Encouraging results have been found in Rohm and Haas' laboratory resin adsorption tests on the stripped condensate produced by the Lurgi coal gasification pilot plant in South Africa. The product water is reportedly suitable for use as high-pressure boiler feed water after deionization and condensate polishing.

References

1. Rohm and Haas Company, "Process for the Recovery of Phenolics from Aqueous Streams," August 1977.
2. Rohm and Haas Company, "Summary Bulletin AMBERLITE Polymetic Adsorbents," 1978.
3. Simpson, R. M., "The Separation of Organic Chemicals from Water," Presented at the third Symposium of the Institute of Advanced Sanitation Research International, April 13, 1972.
4. Lorton, G. A., "Removal of Phenols from Process Condensate," C. F. Braun & Co., Interim Report, October 1977.

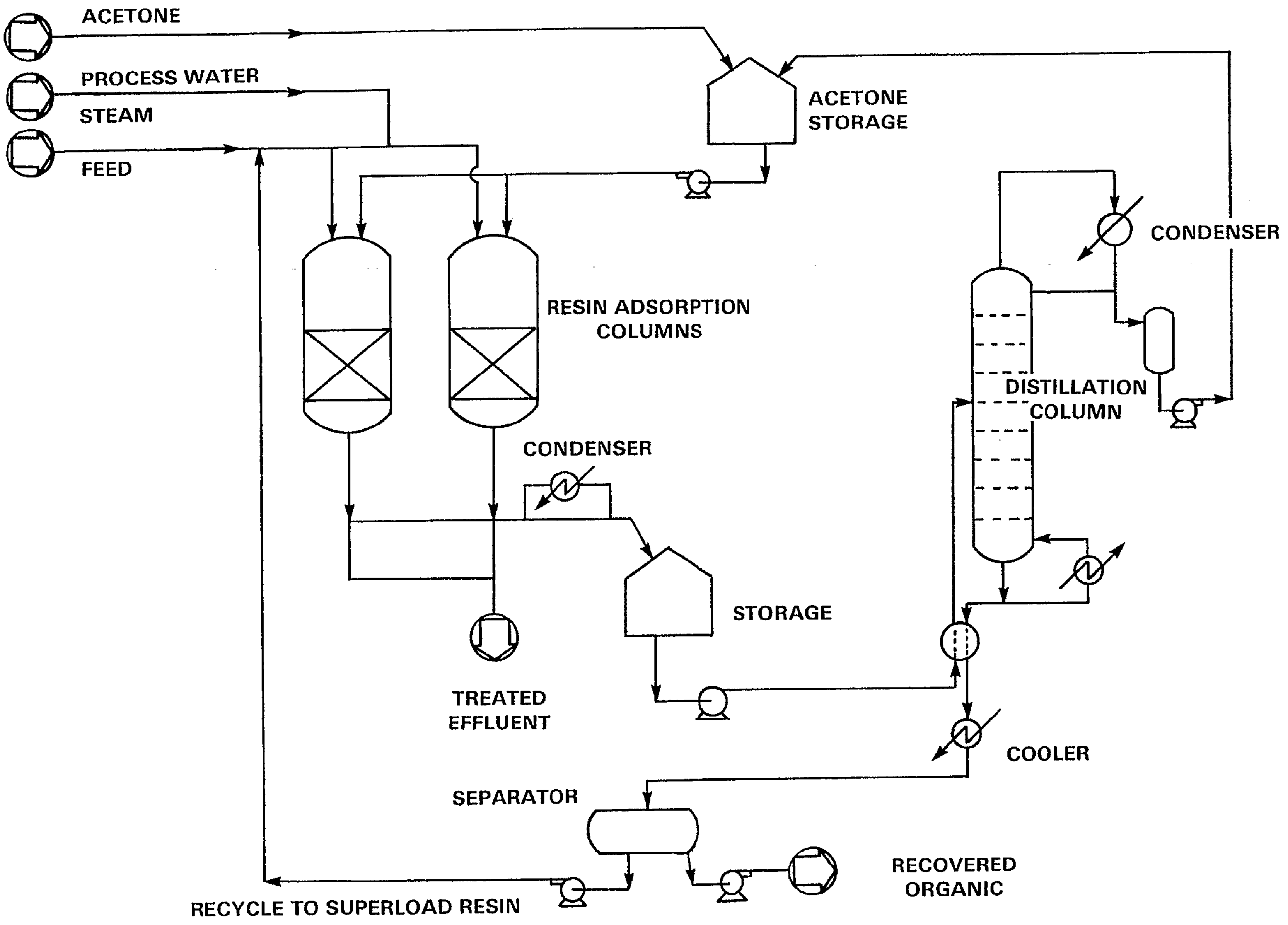

Figure 3C.4-1 Rohm And Haas Phenol Removal Process.

3C.5 TAR REMOVAL

Suppliers

Tar, tar-oil, and other heavy hydrocarbons are usually removed simultaneously along with entrained particulates in a system consisting of scrubbing, cooling, and settling steps, and there is no special process for their removal as such. Solvents used in physical absorption processes for H_2S removal are generally capable of removing tar and other organics. In fact, tar and organics removal is always part of a typical proprietary acid gas removal process. For example, Rectisol (Chapter 3A.17) has a section that is designed for final tar removal and heavy hydrocarbons polishing. Each tar removal system performs somewhat differently with respect to tar and particulates and must be evaluated from information furnished by its supplier.

State of Development

In the past, the practices employed in the coke-oven and by-products industry were used widely for tar removal in all gas manufacturing processes. Most of the tar is condensed from the coke-oven gas in the collecting mains, where the gas is in direct contact with the spray of flushing liquor. In addition to cooling the gas and condensing the tar, the flushing liquor washes tar fog from the gas. The tar and liquor flow to a decanter, where tar is settled and separated from the rest of the liquor. The hot gas, saturated with water, is further cooled in a cooler, where water vapor and the lighter tar fractions are condensed. Tar fog remaining in the gas from the cooler will gradually precipitate throughout the rest of the gas-purification and downstream units unless removed. To prevent the formation of troublesome deposits, the gas is passed through one (or both) of two types of tar extractors - the impingement type and the Cottrell electrical precipitator. In recent years, stringent EPA regulations and the renewed interest in coal gasification have prompted many process suppliers to re-examine acid gas removal, particulates removal, and tar removal problems and modify their processes accordingly. Today there are several processes that simultaneously remove tar and heavy organics together with particulates or acid gasesK The remainder of this chapter examines a typical tar and particulates removal process suitable for gasification application.

General Description

One cannot examine the tar removal without also studying the particulates removal capability of a system. Alternate control technologies commercially available for removing the particulates and tars from the raw gases from a coal gasifier can be classified into the following four generic control technologies: conventional cyclones, venturi (wet) scrubbers, electrostatic precipitators (ESPs), and media filters.

Cyclones use the centrifugal force created by a spinning gas stream to separate particulates from the carrier gas. The advantages of the conventional cyclone are that it is a simple device and a prover technology. However, cyclones suffer from the disadvantage of having low removal efficiencies for particulate sizes less than 5 mm. Because of their relatively low capital and operating costs, cyclones are commonly used as precleaners to remove most of the large aerosol particles in a gas stream upstream of a more expensive control device (e.g., venturi scrubber or electrostatic precipitator) required to remove the smaller particles.

Wet scrubbers are available in a wide variety of designs; all operate on a common principle of contacting a pollutant-laden gas with a liquid (usually water) that captures the pollutants. Wet scrubbers can be used to remove both particulates and tars. All wet scrubbers produce a liquid slurry for disposal or further treatment. Most modern applications attempt to concentrate the wastes to simplify their ultimate disposal, and to recirculate as much of the scrubbing liquid as possible. The collection efficiency of wet scrubbers is strongly dependent on particle size. To achieve high collection efficiencies with small particles, a high energy input is required. Wet scrubbers have been found to be very effective in removing tars from raw product gases. Commercially available gasification systems generally have employed various types of wet scrubbers to quench and cool the gases and knock out the tars, along with a portion of the particles.

The venturi scrubber employs a venturi shaped constriction and high throat velocities to atomize the scrubbing liquid. As with wet collectors in general, the collection efficiency increases with higher pressure drops. Different pressure drops are achieved by designing for various gas velocities in the throat. The collection efficiency of the venturi scrubber can generally be considered highest of the wet collectors.

Electrostatic precipitators (ESPs) for cleaning particulates from gases have also been found to be an efficient means of detarring the gases. ESPs have been used in commercial installations for over 70 years. ESPs operate by using a high-voltage direct current to create gas ions that impart an electrical charge to particulates by bombardment. The charged particles are collected by exposing them to an electric field, which causes them to migrate and deposit on electrodes of opposite polarity. The electrode cleaning system is dependent upon the type of precipitator. The conventional dry-type precipitator collects particulates on a dry electrode and removes them periodically by mechanical shaking or rapping. The new wet-type precipitator collects and removes particulates with a thin, continuous flowing film of water. The operating temperatures are generally less than 150 °F.

Media filters include fabric (baghouse) filters and granular bed filters. The collection takes place by the impaction of particles on the filter media and by particulates' being collected in the interstices of the filter. After the initial collection at the filter surface that produces a filter cake, further collection is accomplished essentially by cake sieving. Media filters can achieve a very high collection efficiency (99.99%) even for submicron particles. However, a media filter should not be employed for gases containing high levels of liquid or sticky particles (e.g., tars). Thus, fixed-bed gasifiers, in particular, may not be compatible with fabric filters because of the quenching operation commonly used to condense and remove tars and oils.

The choice of gas quenching and cooling processes to be used depends upon the nature of the hot raw gas and the down-stream processing. Waste heat recovery is always desirable, but fouling problems caused by tar and oil condensation in the waste heat boiler must be considered. In addition, it may be necessary to remove tar and oil constituents from the gas prior to treatment in, say, an acid gas removal process to prevent contamination of the solvent or catalysts. In quenching and wet scrubbing to cool and remove particulates and tars from the hot gas produced in a gasifier, the most common problem is the formation of a stable emulsion, which, in turn, creates a water pollution problem. Therefore, design of the quenching, scrubbing, and decanting system is critical and should be evaluated individually with respect to each gasifier's operating conditions.

A tar decanter is usually a rectangular tank with baffles and weirs built inside. The mixture of tar and liquor enters at one end and flows toward the outlets at the other. In its passage through the decanter, it separates into a lower layer of tar and an upper layer of liquor.

The main components of a low-temperature tars and particulates removal system suitable for gasification application are:

- Gas cooling or quench section - direct cooler or wet/venturi scrubbers.
- Separator - cyclones and electrostatic precipitators (ESPs) to remove particulates and condensates from fuel oil.
- Tar separator or decanter - to separate tars or solids from flush liquor or slurry.

A simplified block diagram depicting a typical tar/particulates removal system is shown in Figure 3C.5-1.

The tars and heavy organics removal feature incorporated in various physical absorption processes is mainly designed for removal of remaining trace tars or final organics polishing. For design specifics and capability, one should refer to sections on these processes in this Handbook.

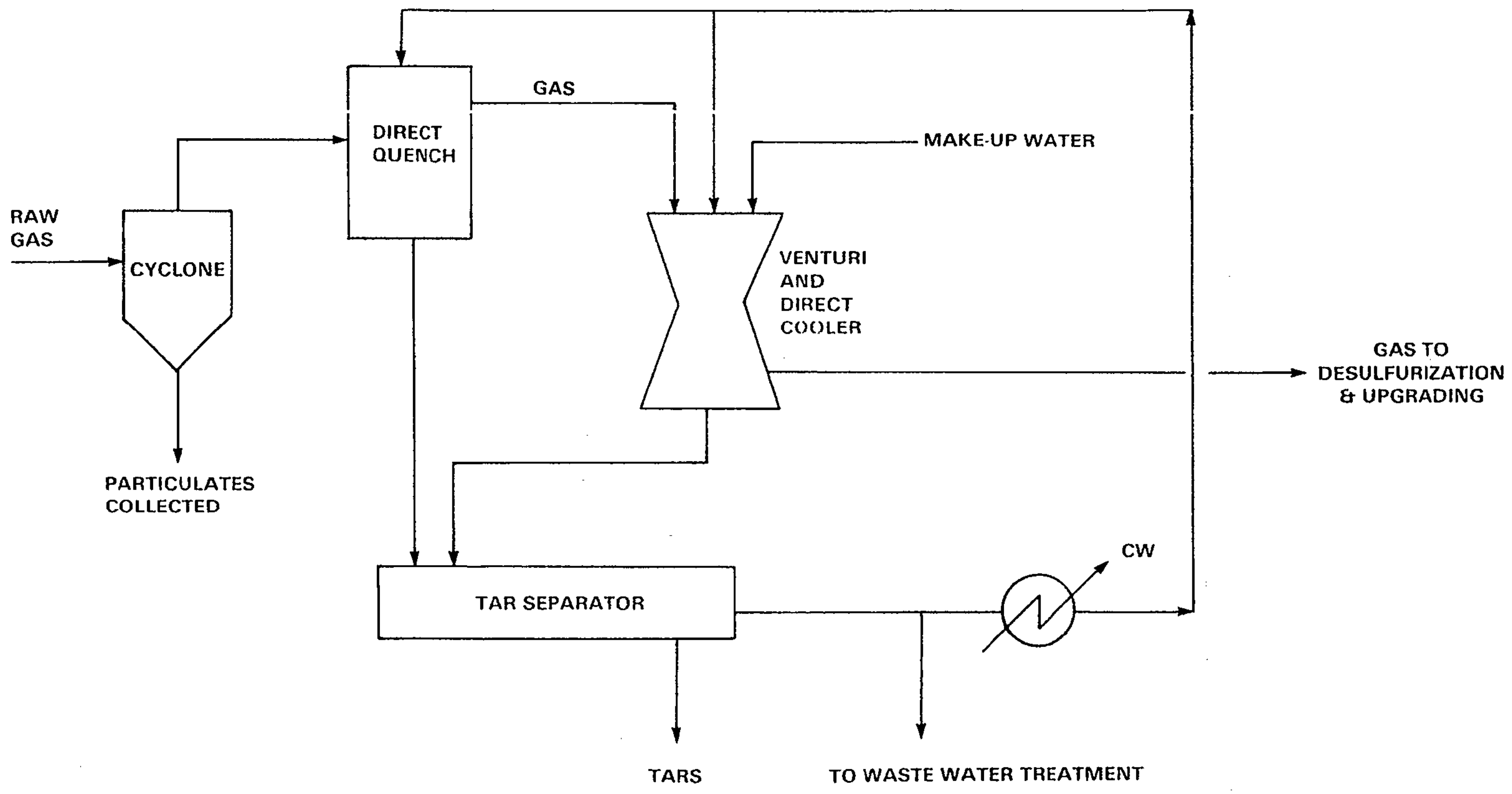

Figure 3C.5-1 Simplified Tar/Particulates Removal System.

4.1 AIR PRODUCTS CRYOGENIC SEPARATION

A/E
Air Products and Chemicals, Inc.
P.O. Box 538 T
Allentown, PA 18105

State of Development

Cryogenic separation is one of the principal methods for purifying H_2, CO, and synthesis gas (H_2 + CO) and recovering light hydrocarbon by-products.

Early cryogenic systems were used primarily for high tonnage oxygen and nitrogen production. In recent years, these methods have also been used to produce a 90-95% hydrogen[1] from ammonia synthesis gas, refinery off-gases, and off-gas from certain petrochemical operations. The Air Products cryogenic process can be used in conjunction with the acid gas treatment processes.

Description[1 2]

Although the cryogenic process has a wide application, the present discussion is limited to its use in hydrogen purification in coal conversion processes and refinery operations.

Several variations are available for the cryogenic purification of hydrogen, depending on the total gas flow, pressure and temperature of the feed, and concentration of light hydrocarbons. Figure 4.1-1 pictures a simplified cryogenic system that illustrates the basic principles involved. Feed gas is compressed to at least 400 psig, cooled, and separated from its condensed moisture in a knockout drum. (Gas is precooled in a refrigeration unit and then cooled to -200 to -335 °F by interchange with the purified hydrogen and light hydrocarbon products.) It then passes through a fixed bed adsorber, where water and any H_2S, CO_2, or NH_3 present in the feed gas are reduced to below 1 ppm. If further cooling is required for the desired separation, the stream passes through another refrigeration unit.

Compact, high-efficiency countercurrent heat exchange equipment is always employed in cryogenic processing units. The processes are characterized by near reversible heat exchange (very small temperature difference between feed and return streams) to achieve maximum use of available refrigeration and minimum external refrigeration supply requirement.

Light hydrocarbons in the feed gas are condensed in the cooling train, and the two-phase mixture is separated. Purified hydrogen passes overhead, while the liquid hydrocarbons are expanded isoenthalpically to provide refrigeration for the feed gas via the Joule-Thomson effect. More than one separating stage is often used if separation of the light hydrocarbons into fractions is desired.

When the concentration of light hydrocarbons in the feed gas is greater than 25%, precooling in a refrigeration unit is generally not required, since sufficient cooling is provided by the Joule-Thomson effect. In most coal gasification processes, however, the gas produced is too low in light hydrocarbons to eliminate precooling entirely. Precooling also makes it possible to reduce adsorber bed size, particularly for water.

Deep level refrigeration (below -150 °F), if required, is normally obtained by turbo-expansion. In some cases, heat pumping is employed in place of external cold level refrigeration.

Operability Limits[2]

Since several operating schemes could be included under the general heading of cryogenic processes, inherent operating limits cannot be sharply defined. However, operating pressures for hydrogen purification usually range from 400 to 1000 psig, while operating temperatures are in the subzero range. Feed gas hydrogen concentrations of 30 to 90 vol% are common. Nitrogen, carbon monoxide, and hydrocarbons through pentanes can be separated easily. Impurities such as water, aromatics, higher hydrocarbons, and acid gases, which can be tolerated only in small quantities, are removed in the adsorber.

Purification Limits[3]

Cryogenic processes are available to produce 99.9% liquefaction grade hydrogen. Refinery off-gases and gases from coal conversion processes, however, do not require this level of purification, since the hydrogen purity desired is normally 90% to 98%.

Partial condensation in multiple phase separators yields mixed products. Sharp separation of recovered hydrocarbon fractions to yield high-purity component products is possible within a cryogenic system if distillation columns are included. The distillation columns, in almost all cases, require a supply of low-level refrigeration for the column condensers - or heat pumping is required to shift thermal duty between reboiler and condenser of the distillation unit.

Utility Requirements

Not available.

Environmental Considerations

If activated carbon or molecular sieves are used as the adsorption medium, absorbent regeneration will produce an effluent gas containing traces of H_2S. The remainder of the cryogenic process does not produce waste effluents.

Remarks

Cryogenic separation is a well proven process for purifying hydrogen and recovering light hydrocarbon by-products. It is more economical when hydrocarbons in the feed gas exceed 25%, since less external refrigeration is required. Special cold box construction is necessary, however, to accommodate the sub-zero temperatures involved.

Equipment inside the cold box is not readily accessible for maintenance. However, cold box units usually employ quality all-welded internal construction, even on valves, permitting many years of operation with no internal maintenance.

References

1. Fisher, T. F., ''Hydrogen Conservation in Refineries via Cryogenic Processing,'' presented at the National Petroleum Refiners Association Annual Meeting, San Antonio, Texas, March 26-28, 1972.
2. ''Cryogenic Methane Separation/Catalytic Hydrogasification Process Analysis,'' Interim Report, Air Products and Chemicals, Inc., Allentown, Pennsylvania 18105, May 15, 1979.
3. Cassano, A.A.; et. al., ''Purification and Cryogenic Separation of SNG Produced from Coal,'' presented at Cryogenic Engineering Conference, 1979.

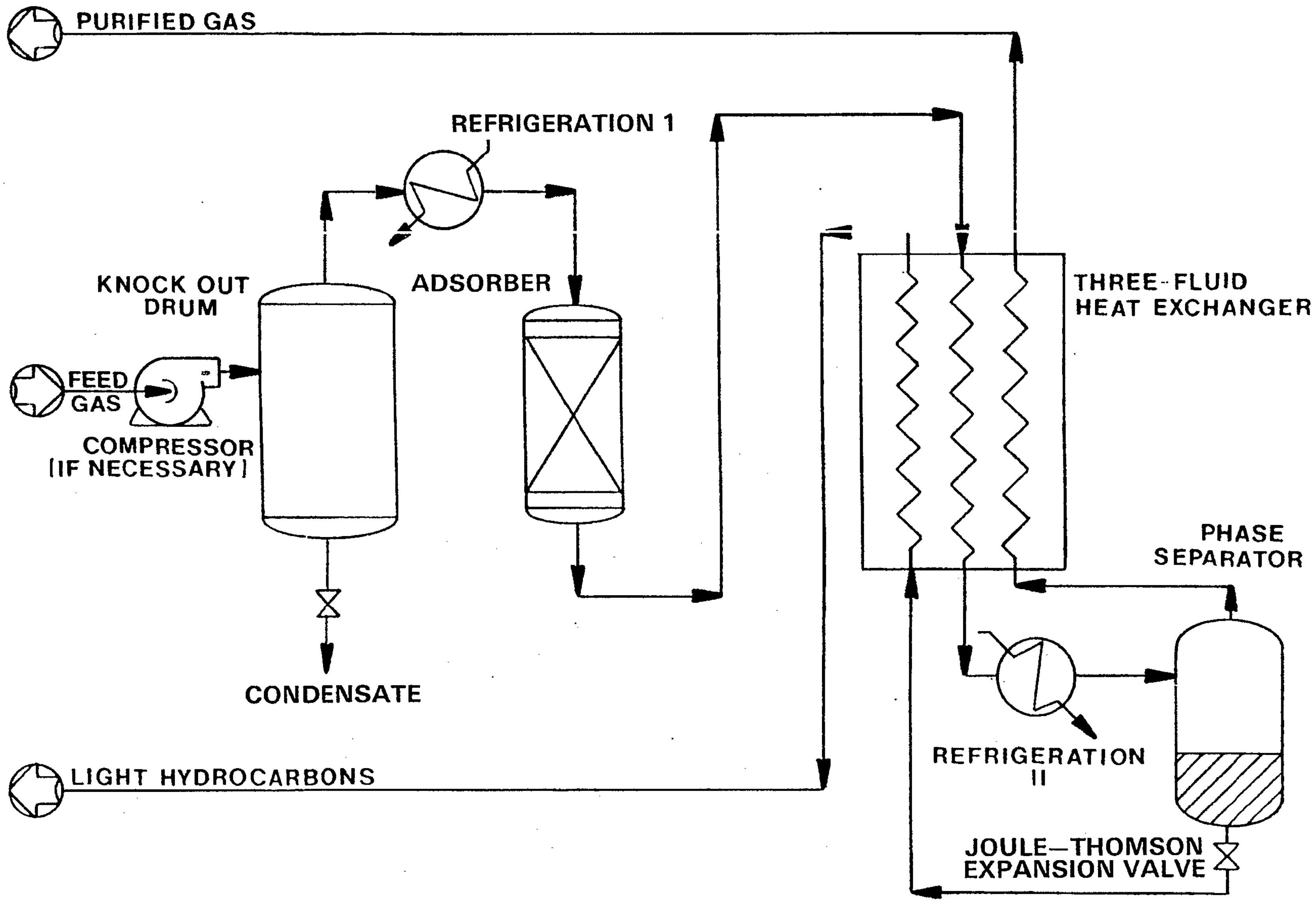

Figure 4.1-1 Air Products Cryogenic Separation

4.2 JOHNSON MATTHEY DIFFUSION SEPARATION

Developer

Johnson Matthey, Inc.
Malvern, PA 19355

State of Development[pc]

Palladium membranes have long been known to selectively allow the diffusion of hydrogen. However, they encountered structural failure (the diffusion phenomenon takes place between 600 °F and 800 °F, but palladium suffers hydrogen embrittlement in heating and cooling through the range of 570 °F to 590 °F). Current technology employs alloys of palladium with silver. Diffusion rates of palladium silver alloys are better than those of the original membranes. (For example, 80 Pd-20 Ag has a permeability rate of 2.46 $ft^3/ft^3/sec$, whereas 99.5 Pd 0.5 Ag has a permeability rate of 1.35 $ft^3/ft^3/sec$.) However, diffusion technology, using palladium-silver, has been used only on nominal flow rates, e.g., 3500 cubic feet per hour.

Process Description[1]

Hydrogen may be extracted from a mixed gas stream. The mixed gas stream fed to a diffusion cell is characterized by its total pressure and by its partial pressure of hydrogen. The extraction efficiency depends upon the proportion of the total throughput of hydrogen that is usefully extracted. The diffusion cell is shown in Figure 4.2-1. It consists of a stainless steel shell able to withstand maximum internal pressures of up to 500 psi and temperatures up to 932 °F. Connection to each cell is made up by means of standard stainless steel pressure couplings. The three couplings of each cell are of the same size to ensure interchangeability of each cell. Impure hydrogen is led to the manifold end of diffusion tubes by means of a central inlet tube within the shell. Hydrogen diffuses through the palladium alloy membrane and emerges as very pure gas. The undiffused hydrogen is carried out of the cell with the bleed. The cell dimensions vary from 0.84- to 1.90-in. O.D. and up to 31-in. length. These cells have not been used in large industrial-scale hydrogen purification.

The relation describing the principle of operation of the diffusion cell is

$$V = K\left(\frac{a}{t}\right) DX, \text{ where}$$

V-volume of hydrogen diffusion per unit time
K-constant
a-membrane area
t-membrane thickness
D-diffusion coefficient
X-concentration gradient

Operability Limits

A silver-palladium diffusion cell typically works at 200 psi and 752 °F.

Purification Limits

Extremely pure hydrogen (less than 0.5 ppm impurities) can be obtained.

Utility Requirements

Electrical power requirement is approximately 0.01 kWh/ft^3 of hydrogen.

Environmental Considerations

The diffusion cell is totally enclosed and presents no environmental impact.

Remarks

Scale up of present technology to large flows (required by coal gasification plants) does not appear feasible. A large amount of alloy material would be required. (For example, 20 oz of alloy would be needed to service a flow of 500 ft^3/hr.) Some advantage can be gained by using a silver-palladium diffusion cell to generate pure hydrogen for gas chromatograph carrier gas (rather than using helium) and other medium- to small-scale uses including semiconductor manufacture and refractory metals processing.

References

1. Conner, H., "Palladium Alloy Diffusion Cells," Platinum Metal Review, October 1962, p. 131.

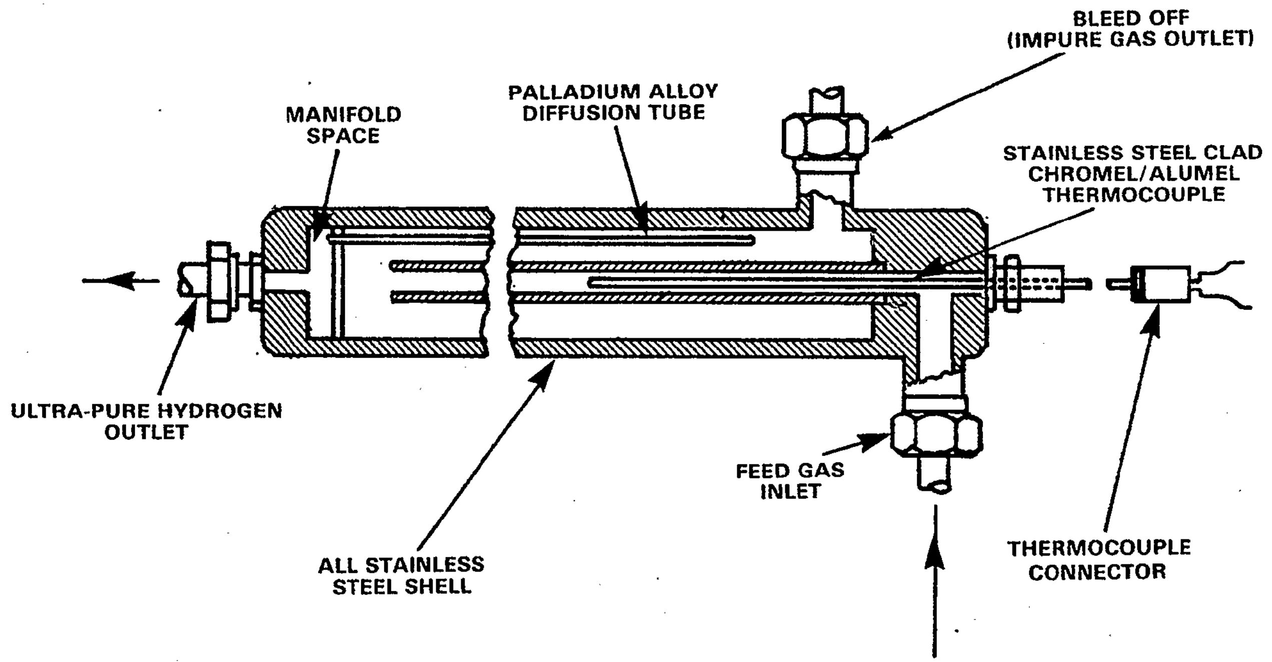

Figure 4.2-1 One Type of Johnson Matthey Diffusion Cell.

4.3 LEAN OIL WASH

Supplier

Virtually all engineering firms active in the petroleum industry offer the lean oil wash process.

State of Development

Variations of the basic lean oil wash process have been used successfully in petroleum refineries and coal-gas plants since the 1880s.[1]

The widest applications are in the petroleum industry for removing methane, ethane, and heavier hydrocarbons from hydrogen-rich, refinery off-gases. Lean oil washes are also commonly used in coke plant operations. Hundreds of units are successfully operating worldwide.

Process Description

This dimension of lean oil absorption processes is limited to their use in hydrogen purification in coal conversion processes and refinery operations. Both light and heavy hydrocarbons are assumed to be impurities in the hydrogen.

The basic lean oil wash process is shown schematically in Figure 4.3-1. Feed gas enters the absorber at the bottom and passes countercurrently to a descending lean oil solvent. Hydrocarbons are physically absorbed in the oil and purified hydrogen passes overhead.

Rich oil, containing dissolved hydrocarbons, flows from the absorber and is heated by interchange with stripper overhead vapors and the hot lean oil. It is then steam heated, reduced in pressure, and flashed into a stripping column to free the dissolved, light hydrocarbons. As the oil descends through the column, it is contacted countercurrently with live stripping steam to free the heavier hydrocarbons dissolvd in the solvent. Stripped lean oil is pumped from the column base and cooled by interchange with rich oil. It is then water cooled in an exchanger and returned to the absorber.

Desorbed hydrocarbons and stripping steam pass overhead and are partially condensed by interchange with the rich oil. The two-phase condensate is decanted, and hydrocarbons are refluxed to the stripper. Decanted water and the partially cooled vapors then enter a water-cooled condenser for final cooling. Condensate is decanted, and light hydrocarbon vapors are disengaged in a separator. Separated hydrocarbon liquid then flows to storage, while wastewater is sent to treatment and disposal. Recovered vapors are usually compressed and used as fuel gas.

Chemical Description

Since hydrocarbons are physically absorbed from the feed gas, chemical reactions are not involved. Lean oil solvents are usually petroleum fractions selected for each application. Selections are based on operating pressure, degree of purification required, and lean oil properties, such as viscosity, vapor pressure, and boiling range. Coal tar oils can also be used, but they tend to become viscous with use and are generally less desirable than petroleum fractions.[1]

Operability Limits[1 2]

Since several operating schemes could be included under the general heading of lean oil washing, inherent operating limits cannot be sharply defined. Absorber operating pressures vary from atmospheric to more than 2250 psig. Similarly, operating temperatures vary with pressure and physical properties of the wash oil, particularly its boiling range and viscosity. Absorption temperatures in the 60 to 100 °F range, however, are common. Feed gas concentrations are not limiting, but high removal efficiencies are sometimes difficult to achieve with light hydrocarbons.

Stripper pressures vary from below atmospheric to 185 psig, while temperatures range from near ambient to 250 °F. Steam stripping is usually required for low-pressure operation when heavy hydrocarbons are absorbed.

Purification Limits

Proper selection of wash oil solvent and absorber operating conditions usually results in 98% removal of hydrocarbons C_6 and heavier. Removal of lighter hydrocarbons requires high operating pressures and large solvent recirculation. Purified hydrogen concentrations normally range from 80 to 85% by volume.

Carbon disulfide (CS_2), if present in the feed, is also absorbed by lean oil washing. Removal efficiencies range from 50 to 90%.[1]

Utility Requirements[1]

Utility requirements for a typical coke plant benzol recovery unit processing 1 MM scfd are presented below. Operating conditions are near atmospheric pressure and 100 °F. Removal efficiencies are 88% for light oil and 52% for CS_2.

Steam, lb/MM scf	4,400
Cooling Water, gal/MM scf	1,800
Electric Power, kWh/MM scf	Not Available
Oil Circulation, gal/MM scf	11,160

Environmental Considerations

Water condensed in the stripper overhead will be saturated with dissolved hydrocarbons and must be treated prior to discharge. A small stream of wash oil is often purged from the recirculating oil to control accumulation of heavy hydrocarbons. Its ultimate disposition must be determined for each installation.

Remarks

Lean oil washing is an old and dependable process for removing hydrocarbons from hydrogen. It is not as effective as cryogenic separation if light hydrocarbons (C_5 and lighter) must be removed to very low levels. An aqueous waste stream is produced when stripping steam is used to regenerate the wash oil.

References

1. Riesenfeld, F. C., and Kohl, A. L., "Gas Purification," 2nd Edition, Gulf Publishing Company, Houston, Texas, 1974.
2. Nelson, W. L., "Petroleum Refining Engineering," 4th Edition, McGraw-Hill Book Company, Inc., 1958.

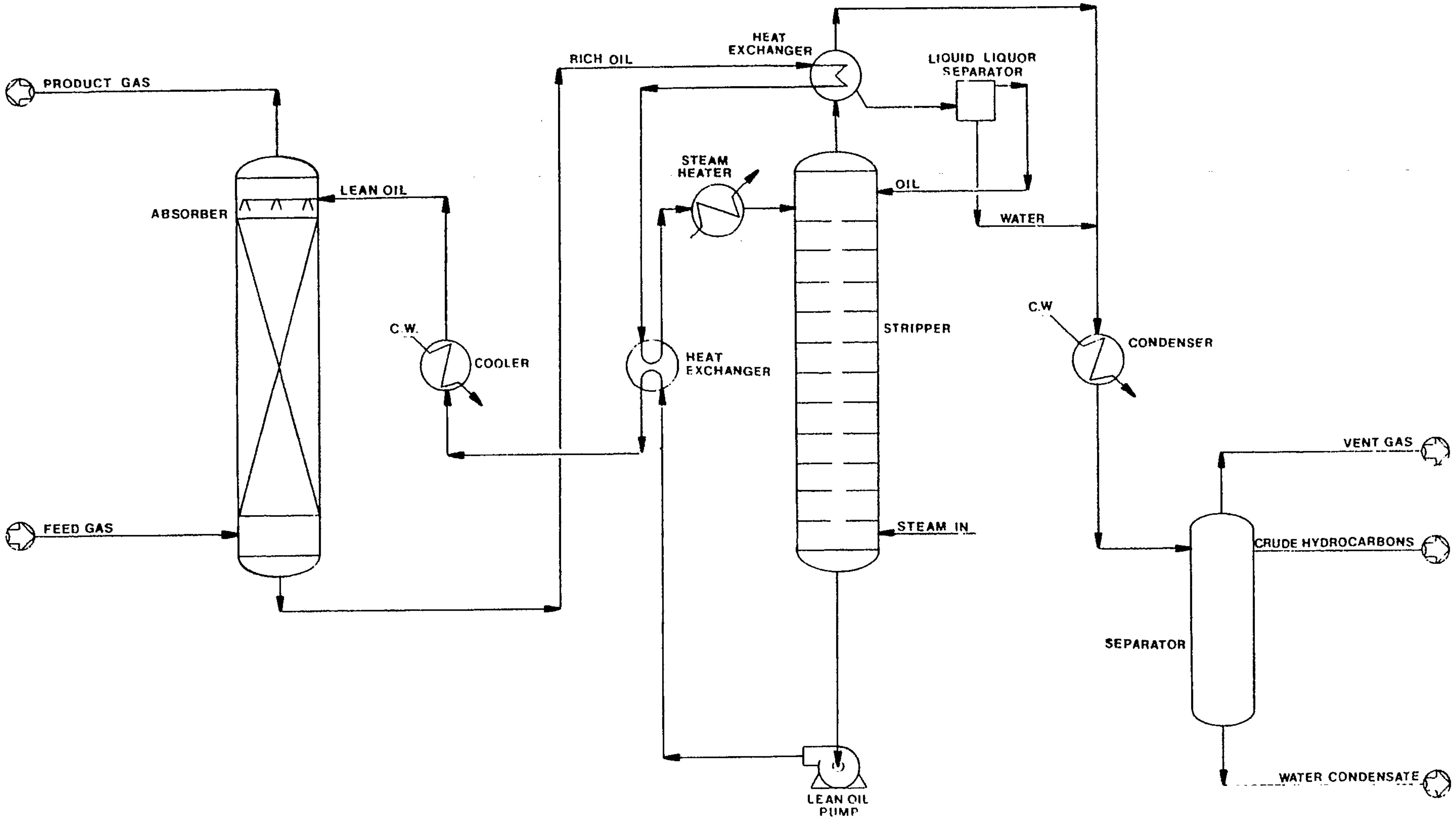

Figure 4.3-1 Lean Oil Wash Process For Hydrogen Purification.

4.4 LINDE/UNION CARBIDE CRYOGENIC SEPARATION

Supplier

Union Carbide Corporation
Linde Division
P.O. Box 44
Tonowanda, NY 14150

State of Development

The upgrading of hydrogen-containing streams by cryogenics has a long history of plant applications. Union Carbide has provided over 40 commercial cryogenic installations, primarily in the areas of petrochemical and C_2+ recovery, helium recovery, ethane recovery, and hydrocracking.[1]

Process Description[2]

Many processes for cryogenic separation and purification are available. The process described here uses a methane wash as part of the cryogenic purification. The process (Figure 4.4-1) is designed to recover a H_2 product gas from a feed syngas and to make separate recoveries of a CO product and CH_4 fuel. The cold box unit operations are:

- partial condensation of feed
- phase separation
- H_2 purification in a high-pressure methane wash column
- CO/CH_4 separation in a low-pressure distillation column
- refrigeration generation
- products compression

The processing scheme consists of cooling the high-pressure syngas in the cold box against returning product streams and a quantity of refrigerant. All the methane and a large portion of the carbon monoxide content are condensed out of the feed gas in this step. The partial condensation process is coupled with phase separation to remove cryogenic liquids at various temperature levels.

The residual H_2 vapor fraction is processed in the wash column. Here the CO content of the H_2 product is reduced -typically to less than 10 ppm - by contacting it with a high-purity liquid methane stream. The wash column bottoms and other condensate streams are then processed in the CO/CH_4 fractionator. The overheads comprise the high-purity CO product. The bottoms stream from this fractionator provides the high-purity methane used as the wash liquid in the first column. A portion of this bottoms stream is used as a low-pressure fuel. Refrigeration necessary to sustain the cryogenic process is provided either by a CO heat pump and expansion cycle integrated with the CO product circuit or by expansion of a portion of the H_2 product stream.

There are two cryogenic methane wash scheme approaches that use either CO heat pump/expansion or H_2 turbo-expansion for the cooling requirements. These approaches can be characterized as:[2]

1. Refrigeration requirements generated by an open-loop, CO heat pump/ expansion loop. Product H_2 is provided at cold box feed pressure minus heat exchanger pressure drop.
2. Refrigeration provided by turbo-expansion of the H_2 product. H_2 product recompression may be required.

Operability Limits

The process operates at approximately 450 psia pressure and at temperatures of 100 °F and below.

Purification Limits[1, 3]

Hydrogen at purities of 99.9% and more can be achieved with carbon monoxide content of less than 10 ppm from a typical syngas feed containing 58% H_2 and 33% CO.

Utility Requirements[2]

For one lb mole of CO product, the total electrical power required is 4.3 kWh and 4.1 kW for approach No. 1 and Approach No. 2, respectively.

Environmental Considerations

Process does not have significant environmental impact.

References

1. "Gas Processing Handbook," Hydrocarbon Processing, April 1979, pg. 160.
2. Davis, J. S., and Martin, J. R., "Cryogenics - The Means for Efficient Synthesis Gas Processing," presented at 86th American Institute of Chemical Engineers National Meeting, Houston, Texas, April 1979.
3. Haslam, A., "Which Cycle for H_2 Recovery," Hydrocarbon Processing, Vol. 51, No. 3, 1972, pp. 101-104.

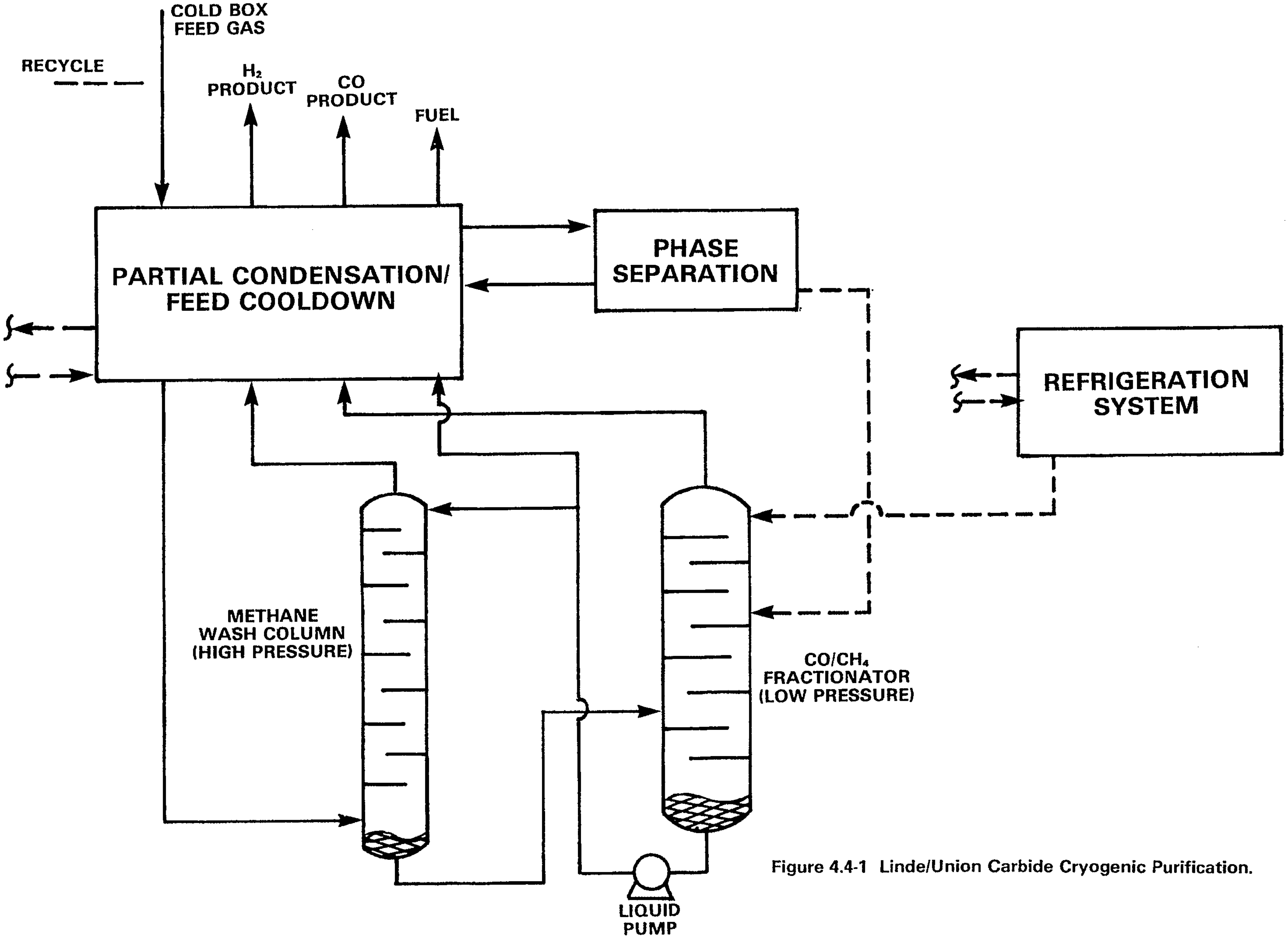

Figure 4.4-1 Linde/Union Carbide Cryogenic Purification.

4.5 LINDE/UNION CARBIDE PRESSURE SWING ADSORPTION

Licensor

Union Carbide Corporation
Linde Division
Engineering Products and Processes
P.O. Box 44
Tonawanda, NY 14150

State of Development[1] [2]

The Pressure Swing Adsorption process (Four-Bed PSA System) was developed by Union Carbide in the early 1960s to purify hydrogen before liquefaction.[1] Linde's PSA units are capable of purifying hydrogen from feed gases containing any or all of the following impurities: NH_3, Ar, H_2O, CH_4, CO_2, N_2, C_2H_6, and C_2H_4. Limited quantities of H_2S, C_2H_2, and C_3 through C_8 can also be removed. These impurities are removed during pressure swing cycles by adsorbents such as molecular sieves, activated carbon, or silica gel. Development of the polybed (ten-bed) system has further enhanced the benefits of the PSA process, especially in steam reforming. It gives higher hydrogen recovery, more efficient use of the adsorbent, and an extension of the range of a single train system to approximately 50 million scfd of hydrogen product.

Feed stocks to these units can be steam reformed hydrogen before or after the water gas shift, demethanizer off-gas, by-product from cryogenic upgraders, dissociated ammonia, and various petrochemical and refinery off-gases. Five polybed plants are in commercial operation (2 in U.S. and 3 in Europe) processing a total feed rate of 190 million scfd; 3 have a feed source from a steam reformer, and the other 2 have feed from methanol loop purge and partial oxidation.

Process Description[3]

Pressure swing adsorption is a single-step process for purification of hydrogen as opposed to conventional methods that require multiple steps. A polybed PSA unit with necessary process and control valves arrangement is shown schematically in Figure 4.5-1. In the PSA process, impurities are adsorbed from the feed gas (by the adsorbent) at a high pressure and then desorbed at a low pressure. The process operates on a repeated cycle having two basic modes, adsorption and regeneration. There is no change in temperature except for that caused by the heat of adsorption and desorption.

Regeneration of the adsorbent is carried out in three separate steps:

- The adsorber vessel is depressurized to a low pressure. Some impurities are removed from the adsorbent during this step.
- The adsorbent is purged with hydrogen to remove the remaining impurities.
- The adsorber vessel is repressurized with hydrogen to feed pressure to be ready for the adsorption step.

The polybed PSA system maximizes hydrogen recovery by effectively using the hydrogen stored in the adsorber vessel at the end of the adsorption cycle to repressurize the other adsorber vessels and to provide hydrogen for purging.

The four-bed conventional units have one bed on adsorption while the other three beds are undergoing various stages of regeneration. In the polybed units, up to three beds are on adsorption simultaneously, thus permitting the use of much higher feed flows (up to 100 million scfd). The cycles of the adsorbers are staggered so that one adsorber at a time comes on line when another completes its adsorption step.

All the PSA units are completely automatic, with start-up and shutdown being push-button operations. After initial start-up, the unit can at once begin operating at full load.

Chemical Description

The PSA process uses (1) molecular sieves, (2) activated carbon, and (3) silica gel. These adsorbents are used either singly or in various combinations, depending upon the impurities present and the type of separation required. Since adsorption is a physical process, no chemical reaction takes place. The feed gas impurities are adsorbed on the surface of the adsorbent bed at elevated pressure. The adsorption process can be reversed by pressure reduction to regenerate the bed.

Operability Limits

A characteristic of a pressure swing cycle is a loss of recovery caused by blowdown and purging losses. The amount of blowdown losses depends on the pressure differential between feed and waste and on the cycling rate. Purging losses are a function of the ratio of the waste pressure to the feed pressure. Higher pressures give high loading up to a point. The economic range for the pressure swing cycle is between 200 and 600 psig. PSA units can yield high-purity hydrogen from a hydrocarbon-rich stream. The PSA units can treat feed with impurities as low as 0.5% to a high of 40% by volume.

Purification Limits[1]

The process typically purifies hydrogen to a 99.999% level from a hydrogen-rich feed stream. A reduction in CO level from 6.0% in the feed to less than 1 ppm by volume can be achieved. From a hydrocarbon-rich feed gas (30% hydrocarbon), the hydrocarbon level can be reduced to less than 10 ppm by volume. For the production of liquefaction grade hydrogen, total impurity levels in the hydrogen are maintained at less than 1 ppm by volume.

Utility Requirements[1]

Utilities required are small quantities of instrument air and power.

Environmental Considerations

Gaseous impurities (such as CH_4, C_2H_4, C_2H_6, CO, CO_2, N_2, NH_3) discharged from the PSA bed during regeneration emerge as a fuel gas stream and are used as a fuel. Exhaust stack gases from these burners are conventionally treated to meet environmental standards.

Remarks

PSA is a physical adsorption process and yields hydrogen of high purity. The process is considered simple and reliable in performance. For the overall control of the polybed PSA process, a programmable controller is used. The controller can be reprogrammed without a process shutdown.

References

1. Stewart, H. A., and Heck, J. L., "Hydrogen Purification by Pressure Swing Adsorption," Adsorption Symposium, 64th American Institute of Chemical Engineers National Meeting, New Orleans, Louisiana, March 16-20, 1979.

2. Heck, J. L., "First U.S. Polybed USA Unit Proves Its Reliability," Oil & Gas Journal, February 11, 1980, pp. 122-130.

3. Union Carbide Corporation, Linde Division, "Hydrogen Purification," Hydrocarbon Processing, April 1979.

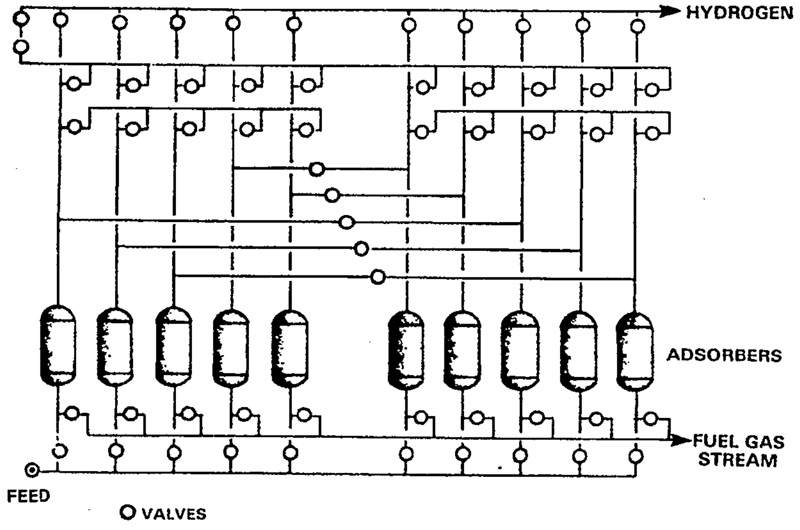

Figure 4.5-1 Linde/Union Carbide Pressure Swing Adsorption Polybed System.

4.6 MATHESON DIFFUSION SEPARATION

Licensor

Matheson Gas Co.
P.O. Box 85
East Rutherford, N.J. 07073

State of Development^{pc}

The Matheson Hydrogen Purifier is a compact instrument designed to provide a continuous supply of very pure hydrogen on a small scale. The level of impurities existing in the hydrogen coming from the instrument is so low that it is nondetectable with known analytical techniques. Five models are available with capacities ranging from 2 to 400 scfh. A 2000 scfh unit has also been built.

Matheson purifiers are ideal for use in laboratories and plants where ultra-pure hydrogen is required for applications involving gas chromatography, metallurgy, electronics, semi-conductors, hydrogenation, catalytic processes, controlled atmospheres, and nuclear research. These units have been on the market since the mid 1970s.

Process Description

The heart of all Matheson Purifiers is the diffusion element -a cell comprised of tubing made from a patented palladium alloy that acts as the diffusion medium. The Matheson Purifier is similar in construction to the Johnson Matthey purifier shown earlier in Figure 4.2-1. In the Matheson Purifier, source gas is brought into contact with the outer surfaces of a palladium alloy tube that acts selectively, passing hydrogen through the tube wall while excluding all other gases. This is achieved by breaking down the hydrogen molecule into atomic hydrogen, which can diffuse through the walls of the palladium tubes and then recombine to the molecular form. Ultra-pure hydrogen is withdrawn from the inner surfaces.

When all piping connections have been made and the power cable plugged in, the unit is operative. The feed gas pressure regulator is set at 200 psig (250 psig maximum), the temperature controller between 700 °F and 750 °F, and the over-temperature cutout at 800 °F maximum. When the temperature reaches the specified reading, the feed gas side of the cell is evacuated by means of a standard laboratory vacuum pump, and the feed gas is admitted. The purifier will then deliver rated flows of ultra-pure hydrogen. Flow can be increased or decreased by varying the input pressure or outlet valve settings.

Installation of an oxygen-removing purifier in the hydrogen line is recommended to protect the palladium diffusion cell. Substantial concentrations of oxygen will reduce catalyst activity and shorten cell life.

Operability Limits

Units are available in 2 to 400 scfh feed sizes and can operate from 50 to 200 psig with a maximum of 250 psig. Start-up time of 20 to 30 minutes is generally required.

Purification Limits

Ultra-pure hydrogen containing 0.5 ppm impurities can be achieved.

Utility Requirements

Smaller models operate on 115 volts, whereas larger models use a 230- to 440-volt, 3-phase power supply. Electric power consumption (kWh): Not Available.

Environmental Considerations

The size of the unit and the diffusional mechanism employed assure operation in an environmentally safe manner.

Remarks

It is doubtful that the palladium alloy tubes would be applicable to large commercial installations because of inlet feed gas purification treatment requirements as well as high tube costs.

4.7 MONSANTO PRISM® SEPARATORS

Developer

Monsanto Company
800 N. Lindbergh Blvd.
St. Louis, MO 63166

State of Development

Monsanto has developed a proprietary system for the selective separation of hydrogen from process or purge gas streams. This system, containing PRISM® Separators, uses the principle of selective gas permeation through membranes to separate hydrogen from other gases. PRISM® Separators have been used for hydrogen recovery from an ammonia synthesis purge gas stream, from petrochemical hydrogenator purges, and from a refinery hydrodesulfurizer purge stream. This technique was first commercially applied in 1977 to adjust the carbon monoxide-hydrogen ratio to meet the stoichiometric requirements of a continuous oxo-syngas process reaction.

The potential of the polymeric membranes used in the process has been proven in various commercial installations within Monsanto and in demonstration (pilot plant) tests in a number of refinery and chemical synthesis operations outside Monsanto.[1] [2]

Process Description

The process is based on the separation properties of a proprietary multicomponent polymeric membrane. The membranes are in the form of hollow fibers. The design of the separator resembles a shell and tube heat exchanger. A bundle of hollow fibers is sealed on one end and embedded in a tube sheet at the other. The entire bundle is encased in a shell with suitable connections, as illustrated in Figure 4.7-1. Pressurized feed gas enters the separator on the shell side and flows axially along the fiber wall. As the gas flows along the fiber surface, "fast" gases (e.g., H_2, He, H_2S, CO_2) respond to the partial pressure differential between the outer and inner surface of the fiber and begin to permeate through to the bore side.

The hydrogen-rich permeate gas leaves the bottom of the separator at reduced pressure. The non-permeate gases ("slow" gases) having high inert concentrations (e.g., CH_4, N_2, Ar) exit the separator from the shell side at essentially the same pressure as the entering feed gas. Composition of the product is controlled by proper selection of space velocity to the membrane surface. Highest hydrogen purity is obtained by high flow rate over a small membrane surface area. Conversely, highest hydrogen recovery is achieved by low flow rate over a large membrane area. Each system is custom designed to meet the specific application requirement of maximum hydrogen recovery or maximum hydrogen purity or the needed combination of hydrogen recovery and purity. Each gas entering the separator has a permeation rate that is characteristic of its ability to dissolve in, and diffuse through, the hollow fiber membrane. PRISM® separation systems operate most efficiently in mixed feed streams made up of "fast" gases and "slow" gases. The system will operate in the presence of various contaminants, such as water, that poison or hamper other methods of gas separation.

Operability Limits

Monsanto PRISM® separators are capable of operating at differentials of 120 psi to 1650 psi between inlet gas pressures and permeate pressures. Maximum feed stream pressure limit is 2150 psi. Units having feed rates of up to 12 million scfd have been sold. The systems have no maximum flow rate design point. Incremental separator surface area can be provided to handle large stream quantities. Systems for streams as large as 750 MM scfd have been designed. H_2 recovery is generally 85-90% but can be increased to 95% by additional separator surface (at a sacrifice in purity) or providing additional partial pressure driving force. These units can operate within a temperature range of 32 to 140 °F.

Purification Limit[1] [3]

The membrane selectivity separates hydrogen from a feed stream and normally yields a hydrogen purity between 86 and 96%. Higher purity can be achieved at the expense of reduced recovery and vice versa. System product purity and recovery rate are designed to meet specific customer requirements.

Utility Requirements

PRISM® separators are driven by the existing stream hydrogen partial pressure. If this is not sufficient, additional compression is necessary to achieve economical separation. Data on this are not available.

Environmental Considerations

The unit operates in an environmentally safe manner.

Remarks

Monsanto's oldest commercial installation has been onstream for four years with no significant changes observed in hydrogen recovery or purity capabilities. The PRISM® separator system has proven to be a simple, reliable, and maintenance-free hydrogen recovery unit.

References

1. "Simple Separation Systems for Hydrogen Recovery," Bulletin, Monsanto Company, 1979.

2. Maclean, D. L., et. al., "An Energy Saving Program in a 600 Short Ton Per Day Ammonia Plant," presented at American Institute of Chemical Engineers 72nd Annual Meeting, San Francisco, California, November 1979.

3. Maciula, E. A., "High H_2 Purity is Key in New Refining Era," Oil and Gas Journal, May 26, 1980, pp 63-68.

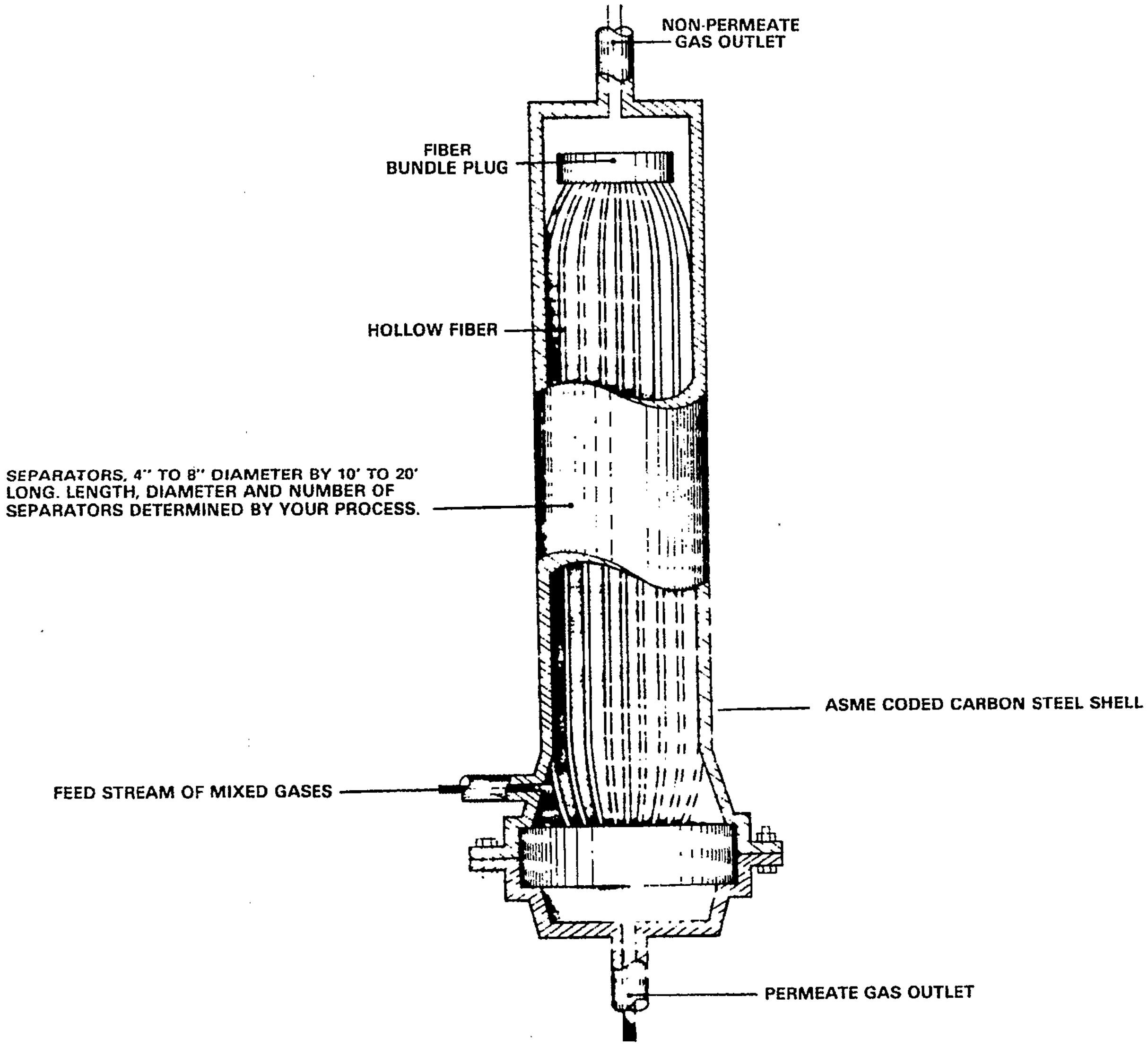

Figure 4.7-1 PRISM Separators.

4.8 PETROCARBON CRYOGENIC SEPARATION

Licensor

Petrocarbon Development, Inc.
P.O. Box 58249
Houston, Texas 77058

State of Development

Cryogenic hydrogen recovery has been successfully applied to the loop purge gas in ammonia synthesis plants, refineries, and petrochemical plants. The object of the purge gas hydrogen recovery system is to recycle as much of the hydrogen and nitrogen present while rejecting the methane and argon inerts Petrocarbon has to date 14 ammonia plant purge gas hydrogen recovery units in various stages of construction and/or operation. These include[1]

Vistron Corporation	Lima, Ohio
American Cyanamide	Fortier, Louisiana
Agrico	Blytheville, Arkansas
Agrico	Donaldsonville, Louisiana
Agrico	Verdigris, Oklahoma
CIL	Sarnia, Ontario
CF Industries	Donaldsonville, Louisiana

The Vistron unit was commissioned in April 1977 and in 18 months developed a 70 stpd increase in ammonia production while processing 420,000 scfh of purge gas.[2]

Eleven units have also been built for refinery and petrochemical applications.[1]

Process Description[1] [2]

This process is generally used in conjunction with an ammonia production plant. Its purpose is to separate the H_2 and N_2 components from the ammonia loop purge gas for recycle back to the ammonia synthesis loop. The basic process shown in Figure 4.8-1 is designed to produce a 90% hydrogen-rich recycle gas stream having less than 1.4% of argon plus methane. The purge gas from the ammonia synthesis plant enters the bottom of a water absorption column, where the ammonia is absorbed and the liquid bottoms sent to the ammonia recovery tower. The separated anhydrous ammonia product is drawn off the top of the tower, while the aqueous ammonia is recirculated back for wash water feed in the absorber after heat exchange with the absorber bottoms.

The ammonia-free gas passes from the absorber to a set of molecular sieve absorbers that remove any remaining trace of the NH_3. The resulting gas, consisting of H_2, N_2, Ar, and CH_4, now enters the cryogenic unit, where ammonia refrigeration is used to partially condense the gaseous products. The two-phase mixture enters a separator, where the liquid fuel gas is separated from the purified gaseous hydrogen product.

The liquid is vaporized through an expansion valve to a lower pressure, and the Joule-Thomson expansion effect is used to cool the inlet purge gas stream from the adsorbers. Increases in hydrogen concentration results in decreasing Joule-Thomson expansion cooling capabilities. This may necessitate additional auxiliary cooling, provided by the ammonia refrigeration loop. The efficiency of the hydrogen recovery in the cold box decreases with increased pressure of the fuel gas.

Operability Limits[3]

The system is designed to accommodate a wide range of operability limits. The ranges for temperatures, pressures, and gas compositions for the raw synthesis gas and the loop purge gas are as follows

Mole %	Feed Gas to Synthesis Loop	Loop Purge Gas
H_2	73-76	60-65
N_2	23-25	19-22
Ar		3-5
CH_4	0.8-1.5	7-10
NH_3	NIL	1.5-3.0
Temperature (°F)	100	-10 to 60
Pressure (psig)	approx. 400	approx. 2200

The ranges for temperatures, pressures, and gas compositions in the hydrogen recovery plants are as follows

Mole %	Hydrogen-Rich Product	Fuel Gas
H_2	90	10-15
N_2	8.5-9.0	40-50
Ar	0.7-0.9	9-14
CH_4	0.3-0.6	25-33
Temperature (°F)	approx. 60	approx. 80
Pressure (psig)	1000	25 to 60

Purification Limits[3] [4]

The process can achieve an approximate 90 volume% hydrogen-rich product from an entering loop purge gas feed of 63 volume% H_2. The H_2-rich product, however, contains acceptably small amounts of Ar and CH_4 (1.0 to 1.5 volume%), which are recycled back to the synthesis loop. The overall cold box hydrogen recovery decreases from 95% to 91% as the fuel gas pressure increases from 25 psig to 60 psig.

Utility Requirements[2] [4]

These hydrogen recovery plants are suitable for purge gases on single and multiple train ammonia facilities, where a single train capacity is 1150 stpd. The following table gives the capacity and utility data for two plant sizes, assuming a normal feed gas composition. These data assume that recovery of anhydrous ammonia has been incorporated in the process.

Ammonia Plant Capacity (stpd NH_3)	1,150	2,300
Ammonia Purge Gas Flowrate (scfh) (i.e., capacity of Hydrogen Recovery Plant	350,500	701,000
Power Consumption (kWh -average)	55	95
Cooling Water (gpm at 15 °F rise)	200	390
Steam (lb/hr - 550 psig for NH_3 recovery)	1,400	2,700
Molecular Sieve (lbs of 5A every 4 years)	3,700	7,200
Nitrogen, Dry, Oil-Free (scfh)	200	200
Instrument Air (scfh)	2,000	2,000
Refrigerant (Btu/hr at -27 °F)	25,000	35,000

Environmental Considerations

Recycling the gaseous and the liquid streams curtails the adverse environmental effects. The effluent streams meet environmental standards.

Remarks

The data presented here are based on an ammonia plant purge gas composition that produces a specific mixture (NH_3, H_2, N_2, Ar, CH_4) of varying concentrations. The cryogenic system is designed specifically to separate out the hydrogen-rich product for recycle back to the ammonia synthesis loop at minimum extra refrigeration requirements.

Petrochemical plants, refineries, and coal synfuel plants will have different requirements for the degree of hydrogen purification needed for recycle. The design and operation of the cryogenic system will therefore have to be modified accordingly.

References

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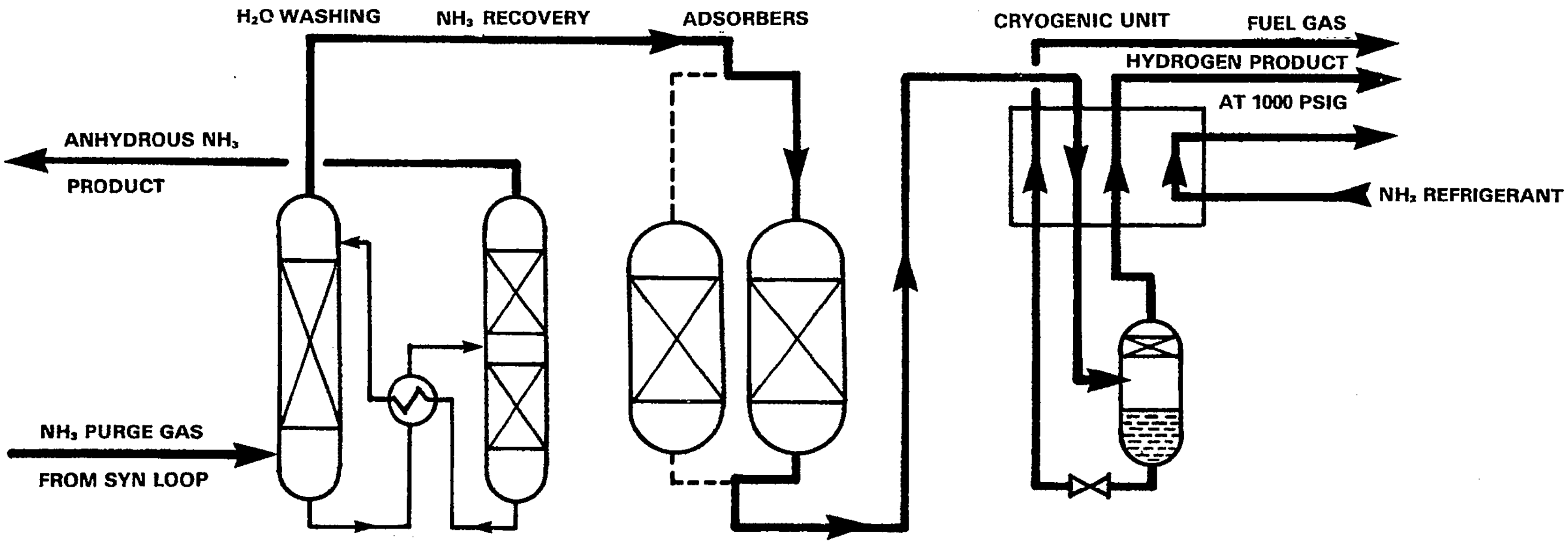

Figure 4.8-1 Petrocarbon Cryogenic Separation.

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